

Docket No.: 29827/42263  
(PATENT)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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In re Patent Application of:  
Ulrich Riegel et al.

Application No.: 10/589,727

Confirmation No.: 9526

Filed: August 17, 2006

Art Unit: 1796

For: Swellable Hydrogel-Forming Polymers  
Having High Permeability

Examiner: Michael L. Leonard

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**APPEAL BRIEF**

MS Appeal Brief - Patents  
Commissioner of Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

This Appeal Brief is submitted in accordance with 37 C.F.R. § 41.37 and MPEP § 1205.02 to support the Notice of Appeal filed in this application on December 3, 2010. This Appeal Brief is accompanied by the fee for filing an Appeal Brief under 37 C.F.R. § 1.17(b) and a one-month extension of time under 37 C.F.R. § 1.136(a). Accordingly, this Appeal Brief is timely filed and no further fees are believed due.

Any additional required fees may be charged, or any overpayment credited, to Deposit Account No. 13-2855.

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### **III. REAL PARTY IN INTEREST**

The real party in interest in this appeal is BASF Aktiengesellschaft (BASF), Ludwigshafen, Germany, the assignee of the entire right, title, and interest to the above-identified application. The assignment was recorded in the United States Patent and Trademark Office (USPTO) at Reel 19861, Frame 0039 on September 13, 2007, which constitutes the entire chain of title from the inventors to BASF.

**IV. RELATED APPEALS AND INTERFERENCES**

There are no related appeals or interferences known to appellants, appellants' legal representative, or the assignee which will directly affect or be directly affected by, or have a bearing on, the Board's decision in the appeal.

**V. STATUS OF CLAIMS**

**A. HISTORY**

This application was originally filed with claims 21.

**B. CURRENT STATUS OF CLAIMS**

Claims added: 22-27.

Claims cancelled: 18-22.

Claims withdrawn from consideration, but not cancelled: None.

Claims pending: 1-17 and 23-27.

**C. CLAIMS ON APPEAL**

The claims on appeal are claims 1-17 and 23-27.

## **VI. STATUS OF AMENDMENTS**

Appellants filed a response to a final Office Action on November 2, 2010. The response was entered, and an Advisory Action was mailed November 17, 2010. No amendment or response was filed in response to the Advisory Action of November 17, 2010. A Notice of Appeal was filed on December 3, 2010. Appellants understand that the current form of the claims is represented by the Response to Office Action, filed November 2, 2010, and as reproduced in the Claims Appendix below.

## VII. SUMMARY OF CLAIMED SUBJECT MATTER

The present invention is directed to swellable hydrogel-forming polymer particles having at least one hydrophilic polymer of dendritic structure (dendritic polymer) and at least one water-insoluble phosphate present on the surfaces of the particles.

Example 5 provides an excellent description of the invention recited in independent claim 1 and the dependent claims. In particular, the example discloses the preparation of superabsorbent (SAP) particles from a monomer solution containing partially neutralized acrylic acid (specification, page 19, line 41 through page 20, line 6). The SAP particles are dried, then sized to a desired particle size range by sieving (specification, page 20, lines 8 and 9). The SAP particles then are postcrosslinked, wherein the postcrosslinking solution contains a dendritic polymer (BOLTORN H-40) and tricalcium phosphate (specification, page 20, lines 29-36). The postcrosslinking solution is sprayed onto the SAP particles to position the dendritic polymer and water-insoluble phosphate on the surfaces of the SAP particles (specification, page 20, lines 40-41). The dendritic polymer and water-insoluble phosphate also can be applied to the SAP particle surfaces in the same manner in the absence of a surface postcrosslinker (specification, page 5, lines 30-35, for example).

Postcrosslinked SAP particles are illustrated in the attached exhibit at page A-\_, i.e., page 97 from *Modern Superabsorbent Polymer Technology*, T. Buchholz et al. eds. (1998). Fig 3.9 of page 97 illustrates the position of the dendritic polymer and water-insoluble phosphate on the surfaces of the SAP particles, with or without surface postcrosslinking.

More particularly, independent claim 1 recites swellable hydrogel-forming polymer particles comprising (a) hydrogel-forming polymer particles (specification, page 8, line 27 through page 9, line 3), (b) at least one hydrophilic polymer of dendritic structure, (specification, page 3, line 42 through page 4, line 4), and (c) at least one water-insoluble phosphate (specification, page 3, lines 27-33), wherein (b) and (c) are present on the surfaces of particles (a) (specification, page 20, line 29 through page 21, line 6).

Claim 23 recites that the hydrogel-forming polymer particles (a) comprise a partially neutralized polyacrylic acid (specification, page 8, lines 32-35; page 12, lines 9-13; and page 19, lines 42-45).

Claim 2 recites that the hydrophilic polymer of dendritic structure comprises a polyester formed from a polyol and 2,2-dimethylolpropionic acid (specification, page 4, lines

21-29). Claim 3 recites that the hydrophilic polymer of dendritic structure comprises a polypropyleneimine, a polyamidoamine, or a polyesteramide (specification, page 5, lines 4-13).

Claim 25 recites that the hydrophilic polymer of dendritic structure is present on the surfaces of particles (a) from 0.005% to 10%, by weight, of the swellable hydrogel-forming polymer particles (specification, page 5, lines 24-25).

Claim 4 recites that the water-insoluble phosphate comprises a calcium phosphate (specification, page 19, line 31 and page 20, line 38).

Claim 26 recites that the hydrophilic polymer of dendritic structure comprises a polyester formed from a polyol and 2,2-dimethylolpropionic acid and the water insoluble phosphate comprises a calcium phosphate (specification, page 4, lines 21-29, page 19, line 31, and page 20, line 38).

Claim 27 recites that the hydrophilic polymer of dendritic structure comprises a polypropyleneimine, a polyamidoamine, or a polyesteramide and the water insoluble phosphate comprises a calcium phosphate (specification, page 5, lines 4-13, page 19, line 31, and page 20, line 38).

Claim 5 recites that the polymer particles further comprise a powdery additive, a dusty additive, or a mixture thereof (specification, page 7, lines 22-27). Claim 6, which depends from claim 5, recites that the additive comprises a metal salt, a pyrogenic silica, a polysaccharide, a nonionic surfactant, a wax, diatomaceous earth, or mixtures thereof (specification, page 7, lines 27-30). Claim 7, which also depends from claim 5, recites that the additive is present in the form of hollow microspheres which are from 1 to 1000  $\mu\text{m}$  in diameter and whose wall thickness comprises from 1% to 10% of said diameter (specification, page 7, lines 37-42).

Claim 24 recites that the particles are surface-postcrosslinked with at least one surface postcrosslinker (specification, page 13, line 8 through page 14, line 13).

Claim 8 recites that the polymer particles comprise less than 50 weight ppm of particles less than 10  $\mu\text{m}$  in diameter (specification, Examples 4 and 5). Claim 9 recites that the polymer particles comprise less than 50 weight ppm of particles less than 10  $\mu\text{m}$  in diameter after exposure to a mechanical stress (specification, Examples 4 and 5).



Claim 10 recites polymer particles wherein not less than 90% by weight of the particles are between 150 and 500  $\mu\text{m}$  in diameter and which are characterized by a CRC of not less than 25 g/g, an AUL of not less than 22 g/g, and an SFC of not less than  $80 \times 10^{-7} \text{ cm}^3 \text{ sg}^{-1}$  (specification, page 12, lines 34-38 and page 8, lines 1-16).

Claim 11 recites polymer particles wherein not less than 90% by weight of the particles are between 100 and 600  $\mu\text{m}$  in diameter and which are characterized by a CRC of not less than 25 g/g, an AUL of not less than 22 g/g, and an SFC of not less than  $60 \times 10^{-7} \text{ cm}^3 \text{ sg}^{-1}$  (specification, page 12, lines 34-38 and page 8, lines 1-16).

Claims 12 and 13 depend from claim 11, and recite particles wherein not less than 95% (claim 12) or not less than 99% (claim 13) by weight of the particles are between 100 and 600  $\mu\text{m}$  in diameter (specification, page 12, lines 34-38).

Claim 14 recites polymer particles having a CRC of not less than 26 g/g and an AUL of not less than 23 g/g (specification, page 8, lines 8-16).

Claim 15 recites polymer particles having a CRC of not less than 30 g/g and an AUL of not less than 25 g/g (specification, page 8, lines 8-16).

Claim 16 recites polymer particles having an SFC of not less than  $80 \times 10^{-7} \text{ cm}^3 \text{ sg}^{-1}$  (specification, page 8, lines 1-6).

Claim 17 recites polymer particles having an SFC of not less than  $120 \times 10^{-7} \text{ cm}^3 \text{ sg}^{-1}$  (specification, page 8, lines 1-6).

### **VIII. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL**

Whether claims 1, 3-15, 23-25, and 27 would have been obvious under 35 U.S.C. §103(a) over Wada et al. U.S. Patent No. 5,797,893 ('893) in view of Abuelyaman et al. U.S. Patent Publication No. 2001/0020062 ('062 publication), Tomalia et al. U.S. Patent No. 4,507,466 ('466), and Wada et al. U.S. Patent Publication 2004/0048955 ('955 publication).

Whether claims 2 and 26 would have been obvious under 35 U.S.C. §103(a) over the '893 patent in view of the '062 publication, the '466 patent, the '955 publication, and Hult et al. U.S. Patent 5,418,301 ('301).

Whether 16 and 17 would have been obvious under 35 U.S.C. §103(a) over the '893 patent in view of the '062 publication, the '466 patent, the '955 patent, and Goldman et al. U.S. Patent No. 5,562,646 ('646).

For the purposes of the issues on appeal, claims 2-17 and 23-27 are grouped and argued with claim 1.

## **IX. ARGUMENT**

### **A. INTRODUCTION**

Appellants submit that the rejections issued in the final Office Action are in error, and that the present application is in condition for allowance. Appellants respectfully request the Board to review and reverse each obviousness rejection issued in the final Office Action.

### **B. PROPER BASIS FOR A § 103(a) OBVIOUSNESS REJECTION**

A determination that a claimed invention would have been obvious under §103(a) is a legal conclusion involving four factual inquiries: (1) the scope and content of the prior art; (2) the differences between the claimed invention and the prior art; (3) the level of ordinary skill in the pertinent art; and (4) secondary considerations, if any, of non-obviousness.

*Graham v. John Deere Co.*, 383 U.S. 1, 17-18 (1966). Obviousness is determined from the vantage point of a hypothetical person having ordinary skill in the art which the claimed subject matter pertains, who is presumed to have all prior art references in the field of the invention available to him/her. In *re Rouffet*, 149 F.3d 1350, 1357 (Fed. Cir. 1998). Furthermore, obviousness must be determined as of the time the invention was made and in view of the state of the art that existed at that time. *Uniroyal Inc. v. Rudkin-Wiley Corp.*, 837 F.2d 1044, 1050-51 (Fed. Cir. 1988).

The Patent Office must clearly articulate facts and reasons why the claimed invention "as a whole" would have been obvious to a hypothetical person having ordinary skill in the art at least as of the claimed invention's effective filing date. *KSR Int'l Co. v. Teleflex Inc.*, 127 S.Ct. 1727, 1741 (2007) (citing with approval *In re Kahn*, 441 F.3d 977, 988 (Fed. Cir. 2006) ("[R]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness.")); see also MPEP §2143 ("The key to supporting any rejection under 35 U.S.C. §103 is the clear articulation of reason(s) why the claimed invention would have been obvious.").

To reach a proper determination under 35 U.S.C. §103(a), the examiner must step backward in time and into the shoes worn by the hypothetical "person of ordinary skill in the art" when the invention was unknown and just before it was made. In view of all factual information, the examiner must then make a determination whether the claimed invention "as a whole" would have been obvious at that time to that person. Knowledge of appellants'

disclosure must be put aside in reaching this determination, yet kept in mind in order to determine the "differences," conduct the search, and evaluate the "subject matter as a whole" of the invention. The tendency to resort to "hindsight" based upon appellants' disclosure is often difficult to avoid due to the very nature of the examination process. However, impermissible hindsight must be avoided and the legal conclusion must be reached on the basis of the *facts* gleaned from the prior art. MPEP §2142. It is impermissible to use the claimed invention as an instruction manual or "template" to piece together the teachings of the prior art so that the claimed invention is rendered obvious. *In re Gorman*, 933 Fed. 2d 982, 987, 18 USPQ 2d 1885, 1888 (Fed. Cir. 1991). *In re Fritch*, 23 USPQ 2d 1780 at 1784 (Fed. Cir. 1992).

As articulated by the Court of Appeals for the Federal Circuit in *Ortho-McNeil Pharmaceutical Inc. v. Mylan Laboratories Inc.*, 86 USPQ 2d, 1196, 1201-2 (Fed. Cir. 2008):

"As this court has explained, however, a flexible TSM test remains the primary guarantee against a non-statutory hindsight analysis such as occurred in this case. *In re Translogic Tech., Inc.* 504 F.3d 1249, 1257 [84 USPQ 2d 1929] (Fed. Cir. 2007) ("[A]s the Supreme Court suggests, a flexible approach to the TSM test prevents hindsight and focuses on evidence before the time of invention.)."

Furthermore, to establish a *prima facie* case of obviousness, three requirements must be satisfied. First, the prior art references *must* teach or suggest all the limitations of the claims. *In re Wilson*, 165 USPQ 494, 496 (C.C.P.A. 1970). Second, as held in *KSR International Co. v. Teleflex Inc. et al.*, 127 S.Ct. 1727 (2007), "a court must ask whether the improvement is more than the predictable use of prior art elements according to their established functions. ...it [may] be necessary for a court to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person having ordinary skill in the art, all in order to determine whether there was *an apparent reason* to combine the known elements in the fashion claimed by the patent at issue. ...it can be important to *identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements* in the way the claimed new invention does... because inventions in most, if not all, instances rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known." (emphasis added, *KSR, supra*). Third, the proposed modification of the prior art must have had a reasonable expectation of success, determined from the vantage point of the skilled artisan at

the time the invention was made. *Amgen Inc. v. Chugai Pharm. Co.*, 18 USPQ2d 1016, 1023 (Fed. Cir. 1991).

Once the Patent Office properly sets forth a *prima facie* case of obviousness, the burden shifts to appellants to come forward with evidence and/or argument supporting patentability. See *In re Glaug*, 283 F.3d 1335, 1338 (Fed. Cir. 2002). Rebuttal evidence is merely a showing of facts supporting the opposite conclusion." *In re Piasecki*, 745 F.2d 1468,1472 (Fed. Cir. 1984). Evidence rebutting a *prima facie* case of obviousness can include "evidence of unexpected results," *Pfizer, Inc. v. Apotex, Inc.*, 480 F.3d 1348 1369 (Fed. Cir. 2007); or "evidence that the prior art teaches away from the claimed invention in any material respect," *In re Peterson*, 315 F.3d 1325, 1331 (Fed. Cir. 2003). The Patent Office must always consider such evidence supporting patentability. See, e.g., *In re Sullivan*, 498 F.3d 1345, 1352-53 (Fed. Cir. 2007). Comparative data in the specification illustrating the claimed invention must be considered in reaching a conclusion of obviousness. *In re Margolis*, 788 F.2d 1029, 228 USPQ 940 (Fed. Cir. 1986).

In addition, appellants respectfully note that the teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, and not based on appellants' disclosure. *In re Vaeck*, 947 F.2d 4899 (Fed. Cir. 1991). The mere fact that the prior art may be modified in the manner suggested by the examiner does *not* make the modification obvious unless the prior art suggests the desirability of the modification. *In re Gordon*, 733, F.2d at 902, 221 USPQ at 1127. *In re Fritch*, 23 USPQ 2d 1780, 1783-1784 (Fed. Cir. 1992). The Court in *KSR* further emphasized the importance of *identifying a reason* that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does (*Id.*, emphasis added).

**C. REJECTION OF CLAIMS 1, 3-15, 23-25, AND 27 UNDER 35 U.S.C. §103 AS BEING OBVIOUS OVER WADA ET AL. U.S. PATENT NO. 5,797,893 ('893) IN VIEW OF ABUELYAMAN ET AL. U.S. PATENT PUBLICATION NO. 2001/0020062 ('062 PUBLICATION), TOMALIA ET AL. U.S. PATENT NO. 4,507,466 ('466), AND WADA ET AL. U.S. PATENT PUBLICATION NO. 2004/0048955 ('955 PUBLICATION)**

Claims 1, 3-15, 23-25, and 27, directed to swellable hydrogel-forming polymer particles, stand rejected under 35 U.S.C. §103 as being obvious over the '893 patent in view of the '062 publication, the '466 patent, and the '955 publication.

### 1. Disclosure of the '893 Publication

The '893 patent discloses an absorbing agent composition containing an absorbent resin, a water-insoluble inorganic powder, and a polyamine compound (column 5, lines 17-38). Numerous polyamine compounds are disclosed in the '893 patent at column 10, line 57 through column 11, line 59. The '893 patent *fails* to teach or suggest *any* dendritic polymer, and the extensive list of polyamines disclosed in the '893 patent contains *no* dendritic polymers.

The polyamines disclosed in the '893 patent are linear polymers, either crosslinked or uncrosslinked, of the class of polymers I or II shown at attached Appendix page A-25, previously provided to the examiner. The *structure* of the polyamines of the '893 patent are substantially different from a dendritic polymer, and the properties also are substantially different.

It is important to note that the '893 patent states that the polyamine "*must contain*" at least one of a primary, secondary, or tertiary amino group, i.e., a nitrogen containing group ('893 patent, column 10, lines 53-57). It also must be noted that an amino group of an amine, i.e.,  $\text{-NR}_2$ , is different in structure, reactivity, and properties from an amido group of an amide, i.e.,  $\text{-C(=O)NR}_2$ .

The list of polyamine examples of the '893 patent refers to "polyalkyleneimine" and "polyamidopolyamine". However, as explained above, such polyamines have a structure and properties substantially different from a *dendritic* polymer. In a September 28, 2009 response to an Office Action, appellants provided Exhibits A-H showing the structure of a dendritic polymer and how this structure differs from the standard polyamines disclosed in the '893 patent. The extensive Exhibits are not attached for the sake of brevity. In short, the term "polyamine" or "polyamidoamine" defines the functional groups and types of bonding in the polymers, but *not* the *structure* of the polymer. It is well known in the art that different polymer structures lead to different properties.

More particularly, the publication, D.A. Tomalia, *Scientific American*, 272, pages 62-66 (1995), submitted with the amendment of September 28, 2009 as Exhibit B, illustrates the radial structure of a dendritic polymer resulting from the stepwise reactions used to prepare a dendritic polymer. The stepwise preparation of a dendritic polymer also is discussed in the present specification at page 4, lines 10-13. Appellants further provided a technical brochure for BOLTORN<sup>®</sup> dendrite polymers as Exhibit C in the September 28, 2009 amendment, also

attached hereto as Appendix pages A-8 to A-15, which provides another illustration of a dendritic polymer.

## 2. Disclosure of the '062 Publication

The '062 publication discloses dispersants that adsorb to *hydrophobic* particle surfaces (abstract). The hydrophobic particles disclosed in the '062 publication are inorganic compounds, such as insoluble pigments (paragraphs [0059]-[0063]). The dispersant reduces the tendency of *hydrophobic* particles to agglomerate. The '062 publication discloses a "hydrophobic particle" that is nonpolar or has a nonpolar surface ('062 publication, paragraph [0027]). The '062 publication is not remotely directed to *hydrogel* forming polymer particles, which are *hydrophilic* and absorb several times their weight of aqueous media.

Further, the dispersants of the '062 publication are dendritic polymers that have been *modified* by chemical reactions "to attach ionizable moieties and peripheral nonpolymerized nonpolar hydrocarbon hydrophobic moieties" ('062 publication, paragraphs [0031] and [0047] and Fig. 1). See [0081]-[0084] of the '062 publication, wherein the BOLTORN dendritic polymers are highly modified to provide the dispersants of the '062 publication. Importantly, the BOLTORN H30 that is modified in the '062 publication (see '062 publication, paragraph [0053] and paragraphs [0082]-[0083]) is *not* a polyamine, but rather is a polyhydroxy compound free of amino groups (see '062 publication paragraph [0053], structure of BOLTORN H30 in Exhibit C previously provided with Amendment "B" on September 28, 2008 and attached hereto as Appendix page A-10, and in WO 2008/071575, page 5, previously submitted to the examiner as Exhibit B on December 29, 2008).

The dispersants of the '062 publication therefore have a structure substantially different from the dendritic polymer used as a starting material, and neither the modified nor the unmodified dendritic polymer of the '062 publication are polyamines. Further, the '062 publication fails to teach or suggest using a dendritic polymer that has *not* been modified as a dispersant.

## 3. Disclosure of the '466 Patent

The '466 patent is directed to dendritic polymers having increased terminal group densities, and therefore a greater and more uniform reactivity ('466 patent, abstract). The '466 patent discloses preparation of the dense dendritic polymers at columns 7-9. For example, the '466 patent teaches reacting a "polyamidoamine dendrimer" (column 9, lines 29-

30) with an  $\alpha$ ,  $\beta$ -ethylenically unsaturated ester to form a polyester. See the structure in the '466 patent at the top of columns 11 and 12, for example; particularly noting that the polyester contains a plurality of nitrogen atoms as amide and as tertiary amino groups.

The '466 patent therefore merely discloses various dendritic polymers having increased terminal group densities with no suggestion as to their use with hydrogel-forming polymer particles.

#### **4. Disclosure of the '955 Publication**

The '955 publication is directed to a water-absorbent composition. The composition can be used in absorbing products, such as a paper diaper. As discussed below, the '955 publication fails to add anything to the disclosure of the '893 patent, which also is directed to water-absorbent compositions that can be used in a paper diaper.

#### **5. Rejection of Claims 1, 3-15, 23-25, and 27 under 35 U.S.C. §103 As Being Obvious over the '893 Patent in View of the '062 Publication, the '466 Patent, and the '955 Publication**

The basis of this rejection is that the '893 patent discloses an absorbing agent composition containing absorbent organic polymer particles, a water-insoluble inorganic powder, and a polyamine compound, and the '062 publication discloses a dendritic polymer dispersant for inorganic hydrophobic particles. The examiner contends that it therefore would have been obvious to utilize a dendritic polymer of the '062 publication in the absorbing composition of the '893 patent. The '466 patent is cited for disclosing specific dendritic polyamidoamines. The '955 publication adds little or nothing to the '893 patent.

The '062 publication is not even the same field of endeavor as the '893 patent, i.e., hydrophobic inorganic particles vs. hydrophobic organic particles. The '062 publication discloses dispersants that adsorb to *hydrophobic* inorganic particle surfaces (abstract) and prevent the agglomeration of *hydrophobic* particles (paragraph [0027]). The hydrophobic particles disclosed in the '062 publication are inorganic compounds, such as insoluble pigments (paragraphs [0059]-[0063]). The dispersant reduces the tendency of *hydrophobic* particles to agglomerate. The '062 publication discloses a "hydrophobic particle" that is nonpolar or has a nonpolar surface ('062 publication, paragraph [0027]). The '062 publication is not remotely directed to the *claimed hydrogel* forming polymer particles, which are polar, are *hydrophilic*, absorb large amounts of aqueous media, and have polar surfaces. The inorganic hydrophobic particles of the '062 publication are substantially different from



organic water-absorbing particles, in structure and in properties. Further, the dendritic polymers of the '062 publication, which have been modified, are substantially different from the polyamidoamines of the '893 patent, both in structure and in properties.

Appellants fail to see a common sense incentive from the '062 publication for a person skilled in the art to utilize a dendritic polymer in connection with a hydrophilic polymer of the '893 patent. The '062 publication is limited to preventing agglomeration of hydrophobic inorganic particles and provides no reasonable expectation of success when used with hydrophilic polymer particles. In addition, the '062 publication, directed to *modified* dendritic polymers that prevent agglomeration, contains no teaching or suggestion of any effect on the absorbing properties of a polymer. In fact, there could not be any such teaching because the '062 publication is *limited* to hydrophobic particles, i.e., particles that repel rather than attract and absorb water.

Appellants show in the specification that a combination of dendritic polymer and water-insoluble phosphate on a water-absorbing particle surface drastically increases the SFC value of the particles from 33-35 to 62. Appellants specifically point to Table 1, at page 22 of the specification, wherein the *combination* of a claimed dendritic polymer and claimed water-insoluble phosphate (Example 4) provided an unexpected and unpredicted improvement in SFC values over Examples 1-3, which included neither or only one of the dendritic polymer and water-insoluble phosphate. Also see Examples 5 and 6. The dendritic polymer used in the present examples is BOLTORN<sup>®</sup> 40. See previously provided Exhibit B, i.e., WO 2008/071575, pages 4 and 5, and Appendix pages A-8 to A-15, for the structures of a dendritic polymer recited in claims 2, 3, 26, and 27. Such dendritic polymers are not disclosed in the '893 patent *or* the '062 publication. Such an unexpected increase could not have been predicted from a combination of the '893 patent and the '062 publication.

It is noted that for any rationale used by an examiner to support an obviousness rejection, the results of a modification suggested by the examiner must have been predictable. The examiner has failed to satisfy this requirement. In particular, a number of rationales that may be used to support a conclusion of obviousness have been articulated. See *KSR Int'l Co. v. Teleflex Inc.*, 127 S.Ct. 1727, 1739-40 (2007). These rationales are described at MPEP §2143, Eighth Edition, Revision 8 (July 2010). Regardless of the supporting rationale the Patent Office must clearly articulate facts and reasons why the claimed invention "as a whole" would have been obvious to a person at ordinary skill in the art at least as of the

claimed invention's effective filing date. See *KSR Int'l*, 127 S.Ct at 1741; see also MPEP §2143 ("The key to supporting any rejection under 35 USC §103 is the clear articulation of reason(s) why the claimed invention would have been obvious.").

The rationale relied upon by the examiner in this rejection apparently is as follows:

"B. Simple Substitution of One Known Element for Another To Obtain Predictable Results

To reject a claim based on this rationale, Office personnel must resolve the *Graham* factual inquiries. Office personnel must then articulate the following:

(1) a finding that the prior art contained a device (method, product, etc.) which differed from the claimed device by the substitution of some components (step, element, etc.) with other components;

(2) a finding that the substituted components and their functions were known in the art;

(3) a finding that one of ordinary skill in the art could have substituted one known element for another, and *the results of the substitution would have been predictable*; and

(4) whatever additional findings based on the *Graham* factual inquiries may be necessary, in view of the facts of the case under consideration, to explain a conclusion of obviousness.

The rationale to support a conclusion that the claim would have been obvious *is that the substitution of one known element for another would have yielded predictable results* to one of ordinary skill in the art at the time of the invention. *If any of these findings cannot be made, then this rationale cannot be used* to support a conclusion that the claim would have been obvious to one of ordinary skill in the art."

To illustrate the importance of the SFC value in connection with hydrogel-forming polymers, appellants submit concurrently with this response the relevant portions of Goldman et al. U.S. Patent No. 5,599,335 ('335) as Appendix pages A-16 to A-22, which were previously presented to the examiner. This exhibit explains that SFC values demonstrate the permeability of a hydrogel layer formed from hydrogel-forming polymers. The present invention greatly improved this important absorption property of a hydrogel-forming polymer, which could not have been predicted from the cited references, i.e., the '893 patent is silent with respect to dendritic polymers and SFC has *no meaning* for a hydrophobic inorganic particle that does not absorb water.

Further, the dispersants of the '062 publication are dendritic polymers that have been *modified* by chemical reactions "to attach ionizable moieties and peripheral nonpolymerized nonpolar hydrocarbon hydrophobic moieties" ('062 publication, paragraph [0047]). See [0081]-[0084] of the '062 publication, wherein the BOLTORN dendritic polymers (the type used in the present examples, and *claimed* in claims 2 and 26) are *highly modified* to provide the dispersants of the '062 publication. Importantly, BOLTORN H30, either unmodified or modified as in the '062 publication (see paragraphs [0082]-[0083]), is *not* a polyamine, but rather is a polyhydroxy compound free of amino groups (see structure of BOLTORN H30 in Exhibit C previously provided with Amendment "B" on September 28, 2008 in Appendix pages A-8 to A-15). It is noted that the '893 patent teachings *require* a polymer bearing amino groups.

The dispersants of the '062 publication therefore have a structure substantially different from the dendritic polymer used as a starting material, and neither the modified nor the unmodified dendritic polymers of the '062 publication are polyamines. The '893 patent *requires* a polyamine, and accordingly a person skilled in the art would not substitute a *modified* or an *unmodified* dendritic polymer disclosed in the '062 publication for a polyamine of the '893 publication. Further, the '062 publication fails to teach or suggest using a dendritic polymer that has *not* been modified as a dispersant.

In view of the teachings of the '893 patent and '062 publication, a person skilled in the art would not have combined the references in a way that leads to the presently claimed invention. As stated above, a substitution of the polyhydroxy dendritic polymer (modified or unmodified) disclosed in the '062 publication destroys the teachings of the '893 patent which explicitly discloses the *need* for a polyamine. It is submitted that a person skilled in the art would have had no incentive or apparent reason to make this substitution, let alone a substitution using an unmodified dendritic polymer.

Not only does the '062 publication disclose dendritic polymers that do not contain the amino groups that are explicitly taught as necessary by the '893 patent, the '062 publication utilizes a *modified* dendritic polymer to prevent agglomeration of *hydrophobic* particles. The '062 publication defines hydrophobic particles as being non-polar. However, the claimed hydrogel forming particles are *hydrophilic*, i.e., water absorbing. A person skilled in the art therefore would have had no apparent reason to position a modified dendritic polymer of the

'062 publication, or any unmodified dendritic polymer, on a *hydrophilic*, hydrogel-forming particle.

If the examiner contends that a modified dendritic polymer of the '062 publication would be positioned on a hydrogel-forming particle because of the presence of a water-insoluble phosphate, such a substitution would not be made for the reasons set forth above. The '062 publication specifically teaches that a dendritic polymer *must be* modified to perform as a dispersant for a hydrophobic particle. The '062 publication fails to teach or suggest that an unmodified dendritic polymer can perform as a dispersant and the '893 patent requires a polyamine, thus substitution of an unmodified dendritic polymer on a hydrogel-forming particle coated with a water-insoluble phosphate would not provide a predictable result.

Further, it is submitted that in view of the substantial difference in structure and properties between a polyamine disclosed in the '893 patent and a modified or unmodified dendritic polymer, a person skilled in the art would not have substituted a dendritic polymer for the polyamine of the '893 patent with any reasonable or predictable expectation of providing a hydrogel forming particle having improved properties, as disclosed in the '893 patent.

Importantly, a person skilled in the art could not have predicted the unexpected jump in SFC values provided by the presently claimed invention, as demonstrated in Table 1 of the specification, from a combination of the '893 patent in combination with the '062 publication.

It is submitted therefore that a combination of the '893 patent and the '062 publication does not render claims 1, 3-15, 23-25, and 27 obvious. The '466 patent and '955 publication do not cure the deficiencies of the '893 patent and '062 publication. The '955 publication adds nothing to the '893 patent; both are directed to water-absorbing particles. See '893 patent, columns 5-9. The '466 patent merely discloses various *unmodified* dendritic polymers with no suggestion as to their use with hydrogel-forming polymer particles. The dendritic polymers of the '446 patent can be *starting* materials for the modified dendritic polymer of the '062 publication. As discussed above with respect to a combination of the '893 patent and '062 publication, a person skilled in the art would have had no apparent reason or incentive to substitute a dendritic polymer of the '466 patent for the polyamidoamine of the '893 patent.

For all the reasons set forth above, it is submitted that a combination of the '893 patent, '062 publication, '466 patent, and '955 publication fails to render claims 1, 3-15, 23-25, and 27 obvious under 35 U.S.C. §103.

**D. REJECTION OF CLAIMS 2 AND 26 UNDER 35 U.S.C. §103 AS BEING OBVIOUS OVER THE '893 PATENT IN VIEW OF THE '062 PUBLICATION, THE '466 PATENT, THE '955 PUBLICATION, AND HULT U.S. PATENT NO. 5,418,301 ('301)**

Claims 2 and 26, directed to swellable hydrogel-forming polymer particles, stand rejected under 35 U.S.C. §103 as being obvious over the '893 patent in view of the '062 publication, the '466 patent, and the '955 publication, and the '301 patent.

**1. Disclosure of the '301 Patent**

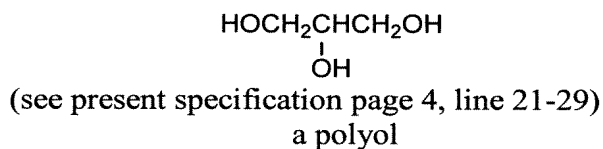
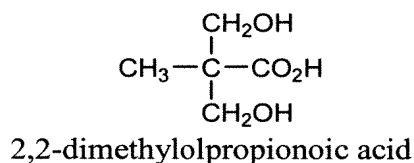
The '301 patent is directed to a dendritic macromolecule having a structure depicted in Fig. 1 of the '301 patent. The dendritic macromolecules contain a plurality of hydroxyl groups and ester groups, but are free of amino and amido groups. The '301 patent fails to teach or suggest using a disclosed dendritic macromolecule with water-absorbing polymeric particles.

**2. Rejection of Claims 2 and 26 under 35 U.S.C. §103 As Being Obvious over the '893 Patent in View of the '062 Publication, the '466 Patent, the '955 Publication, and the '301 Patent**

The '893 patent, '062 publication, '466 patent, and '955 publication have been discussed above. In addition, the patentability of independent claim 1 over a combination of the '893 patent, '062 publication, '466 patent, and '955 publication has been discussed above. The '301 patent does not overcome the deficiencies of these four cited references. The '301 patent is relied upon for a disclosure of the type of dendritic polymer recited in claims 2 and 26. However, a person skilled in the art would not have substituted a dendritic polymer of the '301 patent for a polyamine of the '893 patent for the reasons set forth above in Section C.

With further respect to claims 2 and 26, the Board's attention is directed to the '893 patent, at column 10, lines 53-57, stating that the polyamine "*must contain*" at least one of a primary, secondary, or tertiary amino group, i.e., a nitrogen containing group. This should be compared to a dendritic polymer of the type recited in the claims 2 and 26, and utilized in the examples of the specification, i.e., BOLTORN H-40, and in the '062 publication, i.e., BOLTORN polyols, the structure of which is illustrated in Appendix pages A-8 to A-15, and in Exhibit C previously provided with the Amendment of September 29, 2009.

The dendritic polymer recited in claim 2 and 26 are formed from a polyol and 2,2-dimethylolpropionic acid and has a vastly different structure from the polymer of the '893 patent, e.g., contains *no* nitrogen atoms as amide or amino groups.



These dendritic polymers are neither taught nor suggested by the '893 patent. The '893 patent is silent with respect to the dendritic polymers recited in claims 2 and 26. The '893 patent polyamine *requires* amino-groups. The remaining references provide no apparent reason to substitute a dendritic polymer of claims 2 and 26 (free of amino groups) for the polyamine of the '893 patent. In fact, such a substitution would destroy the teachings of the '893 patent. The explicit teachings of the '893 patent clearly teach persons skilled in the art away from any arguable substitution of a dendritic polymer of claim 2 or 26 for a polyamine of the '893 patent.

In particular, as discussed above, the '893 patent *requires* a polyamine containing amino groups. The dendritic polymer of the '301 patent, and those recited in claims 2 and 26, *do not* contain amino groups. Accordingly, substituting a dendritic polymer of the '301 patent for the polyamine of the '893 patent would destroy the teachings of the '893 patent. The '893 patent teaches away from such a substitution, and any contention that such a substitution would have been obvious in an obvious reconstruction of the claims.

In view of the above, because the '062 publication requires a dendritic polymer that further has been modified, because the '062 publication is directed to *inorganic hydrophobic* particles as opposed to polymeric hydrophilic particles, because the polyamine of the '893 patent is different from a dendritic polymer, because the '893 patent fails to provide any teaching or suggestion that a dendritic polymer could be substituted for a polyamine, because of the unexpected and unpredicted results achieved by the claimed invention, and because of the additional reasons set forth above with respect to an essential polyamine required by the '893 patent, it is submitted that claims 2 and 26 would not have been obvious over a combination of the cited five references.

**E. REJECTION OF CLAIMS 16 AND 17 UNDER 35 U.S.C. §103 AS BEING OBVIOUS OVER THE '893 PATENT IN VIEW OF THE '062 PUBLICATION, THE '466 PATENT, THE '955 PUBLICATION, AND GOLDMAN ET AL. U.S. PATENT NO. 5,562,646 ('646)**

**1. Disclosure of the '646 Patent**

The '646 patent discloses absorbent members for the containment of body fluids, such as urine. The members contain a hydrogel-forming absorbent polymer having specific performance properties. The absorbent member can further contain fibrous materials, such as cotton, kemp, flax, synthetic fibers, etc., as set forth at columns 23-26 of the '646 patent. The '646 patent fails to teach or suggest a dendritic polymer.

**2. Rejection of Claims 16 and 17 under 35 U.S.C. §103 As Being Obvious over the '893 Patent in View of the '062 Publication, the '466 Patent, the '955 Publication, and the '646 Patent**

The patentability of the claims over the '863 patent, '062 publication, '466 patent, and '955 publication has been discussed above. Claims 16 and 17 recite preferred embodiments of the invention. The '646 patent does not overcome the deficiencies of the other four cited references. The '646 patent is relied upon for teaching particles having a high SFC value. However, applicants do not rely solely upon the features of a high SFC recited in claims 16 and 17 for patentability. Applicants do rely however upon all the features recited in claims 16 and 17, *and* in independent claim 1 from which they depend for patentability. Applicants have set forth reasoning why claim 1 is patentable over the cited references, and the '646 patent does not negate the patentability of independent claim 1. It is submitted therefore that claims 16 and 17 are patentable over the cited references for the same reasons independent claim 1 is patentable over these references.

In summary, for the reasons set forth above and with respect to the nonobviousness of claims 1, 3-15, 23-25, and 27, claims 16 and 17 would not have been obvious over a combination of the '893 patent, the '062 publication, the '466 patent, the '955 patent, and the '646 patent.

**F. RESPONSE TO EXAMINER'S REPLY TO APPELLANTS' ARGUMENTS**

In the Final Office Action and in Advisory Action of November 17, 2010, the examiner made statements in an attempt to support the obviousness rejection. Appellants now address some of these statements.

First, the examiner neglects appellants' reasoning that a person skilled in the art would have had no incentive to use a dendritic polymer as a replacement for the polyamine of the '893 patent. As discussed above, the dendritic polymer of the '062 publication is used to prevent agglomeration of hydrophobic inorganic particles; and the '893 patent is directed to hydrophilic, organic particles. So where is the incentive *from the cited art* to make the substitution suggested by the examiner?

Further, how could it have been predicted that a dendritic polymer in combination with a water-insoluble phosphate would increase the SFC value for a hydrogel-forming polymer coated only with *either* a water-insoluble phosphate *or* a dendritic polymer from the mid-30's to the mid-60's for a hydrogel-forming polymer coated with *both* the water-insoluble phosphate and the dendritic polymer (see specification, Table 1 at page \_\_ and compare SPC values of Example 4 ( $62 \times 10^{-7} \text{ cm}^3 \text{ s/g}$ ) to Examples 1-3 ( $33.45 \times 10^{-7} \text{ cm}^3 \text{ s/g}$ ). It is established that for an examiner to rely upon a "substitution" rationale to support a rejection, the results of the substitution must have been predictable.

At paragraphs 11-12 of the Office Action, the examiner states:

"11. In response, it is noted that paragraphs [0053] and [0083] of Abuelyaman et al exemplify dendrimers based on *polyester*, and, therefore, the remaining nucleophilic functional groups are based on polyol. However, this should not be misconstrued as a teaching that the dendrimer of Abuelyaman et al can have *only* hydroxyl groups.

12. Paragraph [0044] teaches that in addition to polyester, the dendritic polymer can be a polyamide, which is commonly known within the art to be the reaction product of polycarboxylic acid and polyamine. One of ordinary skill would understand that when using polyamide instead of polyester, the replacement of polyol for polyamine as the nucleophilic species would result in an amine-functional dendrimer. Thus applicants' position that Abuelyaman et al fail to teach amine-functional dendrimers is not persuasive."

The examiner's reasoning is incorrect. Paragraph [0044] of the '062 publication teaches that the dendritic structure can be any of polyamide, polyester, polyether, etc. However, this is for the *internal* structure of the dendritic polymer. As stated in paragraph [0044], such compounds are "reacted with another compound to provide the *ionic* peripheral groups suitable for use in the invention". Accordingly, the '062 publication does *not* teach amine-functional dendritic polymers, but teaches modified dendritic polymers as explained above. Also note, paragraph [0053] of the '062 publication, wherein the hydroxyl groups can be *reacted* to form succinate groups. The third paragraph of the '062 publication relied upon



by the examiner, i.e., paragraph [0083], teaches the preparation of a stearic acid derivative of a dendritic polymer.

At page 4, paragraph 13, of the Office Action, the examiner states:

"13. Still if applicants maintain that it would not be obvious to *replace* the dendrimers of claims 3 and 27 into Wada et al ('893), the examiner would like to point out that claim 1 merely requires hydrophilic dendrimers (regardless of whether they are modified or unmodified). Therefore, claim 1 is still rendered obvious since, at the least, it would be obvious to combine the composition of Wada et al ('893) with the dendrimers of Abuelyaman et al based on the motivation that the dendritic polymers are useful with water-insoluble compounds — which Wada et al ('893) requires."

First, the dendritic polymer of the '062 publication are useful with *hydrophobic* inorganic particles. The '893 patent is directed to *hydrophilic* organic particles. The examiner has provided no *factual* reasoning to support this suggested substitution, but merely unsupported conjecture. Further, the present claims provide unexpected results that could *not* have been *predicted* from any arguable combination of the '893 patent and the '062 publication.

In addition, the examiner is giving the claims an unreasonably broad interpretation equating a hydrophobic inorganic particle of the '062 publication to the hydrophilic, water-absorbing organic particles of the '893 patent because they are both water insoluble. This is the only property exhibited by these two types of particles, which are different in structure and in properties in all other ways. The examiner also gives claim 1 an unreasonably broad interpretation by including unmodified and modified dendrimers within the scope of claim 1. The '062 publication is clearly directed to modified dendrimers throughout the specification and claims. The present specification fails to teach or suggest a modified dendrimer and would not support a claim directed to a modified dendritic polymer.

Applicants note that the claims are given the broadest *reasonable* interpretation during examination. However, an examiner cannot give the claims an incorrect interpretation. As stated in *In re Skvorecz* (580 F.3d 1262, 1267 (Fed. Cir. 2009)):

"The protocol of giving claims their broadest reasonable interpretation during examination does not include giving claims a legally incorrect interpretation. This protocol is solely an examination expedient, not a rule of claim construction. Its purpose is to facilitate exploring the metes and bounds to which the applicant may be entitled, and thus to aid in sharpening and clarifying the claims during the application stage, when claims are readily

changed. See *In re Buszard*, 504 F.3d 1364, 1366 (Fed. Cir. 2007); *In re Cortright*, 165 F.3d 1353, 1358 (Fed. Cir. 1999).

Also see *In Re Ravi Vaidyanathan* (CAFC 2009-1404, May 19, 2010) stating:

"The PTO Solicitor responds that the broadest reasonable claim interpretation that is supported by the specification is adopted during examination, for the claims can readily be amended during examination, to impart precision if needed. We agree with this protocol as an examination expedient, for its purpose is to aid in sharpening the claims in order to avoid ambiguity or uncertainty in the issued patent. See e.g., *In re Skvorecz*, 580 F.3d 1262, 1267 (Fed. Cir. 2009); *In re Buszard*, 504 F.3d 1364, 1366–67 (Fed. Cir. 2007); *In re Prater*, 415 F.2d 1393, 1396 (CCPA 1969). However, the PTO's "broadest" interpretation must be reasonable, and must be in conformity with the invention as described in the specification.

The Board's interpretation of claim 9 finds no support in the '203 specification, and is not a reasonable interpretation under the rules of claim construction. The description in the specification consistently indicates that the neural network guides the munition all the way intercept. The '203 specification uses the word "strike" synonymously with "intercept," foreclosing the divergent meanings the Board seeks to attach to these terms. The Board's rejection of claims 8 and 9 was based on an incorrect interpretation of these claims. That rejection is vacated and remanded for reconsideration under the correct interpretation of the claims, and in further view of the issues with respect to obviousness as discussed in connection with claims 1–7." (Emphasis added)

The '893 patent and '062 publication are in completely different fields of endeavor. In addition, appellants' specification provides *no* disclosure, and does not support modified dendritic polymers. The examiner's interpretation of claim 1 therefore is unreasonable. It should further be noted that claims 2, 3, 26, and 27 are directed to *unmodified* dendritic polymers.

The examiner's comment that it would have been obvious to substitute the polyamine of the '893 patent with a dendritic polymer of the '062 publication is mere speculation unsupported by the references, but rather destroyed by the '893 patent. As stated above, the two references are not in the same field of endeavor. The '893 patent also explicitly *requires* a polyamine. The '062 publication does not disclose a polyamine, but rather a dendritic polyol (see '062 publication paragraphs [0081]–[0084]). Further, the '062 publication seeks to avoid agglomeration of *hydrophobic inorganic* particles. Hydrogel-forming particles are organic and hydrophilic. Accordingly, the combination of references provides no apparent reason for a person skilled in the art to modify the references in the way presently claimed.

The examiner has failed to provide any factual reasoning that would support the proposed modification.

This is the type of rejection also addressed by the CAFC *In re Vaidyanathan*, May 19, 2010 (2009-1404), wherein in reversing an obviousness rejection sustained by the Board, the court stated the following:

"Obviousness is determined as a matter of foresight, not hindsight. *See id.* at 421 (citing *Graham*, 383 U.S. at 36). *KSR* did not free the PTO's examination process from explaining its reasoning. In making an obviousness rejection, the examiner should not rely on conclusory statements that a particular feature of the invention would have been obvious or was well known. Instead, the examiner should elaborate, discussing the evidence or reasoning that leads the examiner to such a conclusion. Generally, the examiner cites prior art references to demonstrate the state of knowledge. *See* 37 C.F.R. §1.104(c)(2)... In these cases the examiner should at least explain the logic or common sense that leads the examiner to believe the claim would have been obvious. Anything less than this results in a record that is insulated from meaningful appellate review. *Zurko*, 258 F.3d at 1386. If the examiner is able to render a claim obvious simply by saying it is so, neither the Board nor this court is capable of reviewing that determination. *See KSR*, 550 U.S. at 418, citing *In re Kahn*, 441 F.3d 977, 988 (Fed. Cir. 2006) ("[R]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness.").

Because there is insufficient elaboration of the examiner's or the Board's reasoning in this record, we vacate the Board's rejection of claims 1–7. We remand for redetermination of the question of obviousness. On remand, the PTO should determine obviousness based on evidence of record or on the examiner's detailed and articulated reasoning. If there is neither record evidence nor detailed examiner reasoning, the Board should not conclude that Vaidyanathan's claims are obvious."

Claims 2, 3, 26, and 27 recite *unmodified* dendritic polymers. The '893 publication is silent with respect to dendritic polymers. The '062 publication requires a modified dendritic polymer. The '466 patent discloses various dendritic polymers, without *any* disclosure relating to applying a dendritic to a particle. Jumps in logic that require substituting an unmodified dendritic polymer of the '466 patent for the modified dendritic polymer of the '466 patent of the '062 publication (to which the '062 publication is limited), then further substituting the unmodified dendritic polymer for the polyamidoamine of the '893 (which fails to teach or suggest a dendritic polymer) patent can only be justified from a hindsight reconstruction of the claims. Neither substitution is taught or suggested by the combination of cited references, and are contrary to the explicit teachings of the references in combination.

With respect to claim 7, the examiner supports the rejection by stating at paragraph 14 of the final Office Action:

"14. Finally, applicants argue that claim 7 is patentable over the prior art because it would not be obvious to arrive at both the diameter and wall thickness limitations. In response, wall thickness and sphere diameter are two basic parameters used to select the desired type of hollow sphere. The examiner maintains that one of ordinary skill would understand the relationship between both parameters, i.e., achieving the desired density and mechanical strength. Furthermore, applicants have not provided any data showing an unexpected advantage gained when operating at the claimed limitations."

This is bald opinion and a conclusory statement unsupported by the *factual* evidence required to support an obviousness rejection. See the above excerpt from *In re Vaidyanathan*. Further, the cited art completely fails to even teach or suggest hollow microspheres, so claim 7 is allowable for that reason alone. Finally, because the cited art fails to *even* teach or suggest hollow microspheres, no unexpected results are required.

With further respect to claim 7, the examiner reverts to a result effective parameter rationale in the Advisory Action. This is an improper basis to reject claim 7. For an examiner to rely upon a result-effective variable, the variable must be recognized *in the art* as result effective for the variable claimed. The cited art is totally *silent* with respect to hollow microspheres, let alone hollow microsphere of a specific wall thickness and diameter. Accordingly the inclusion of hollow microspheres cannot be termed result effective. See MPEP §2144.05II.B. Further, because the cited art *fails* to teach or suggest hollow microspheres, claim 7 cannot be rejected as being obvious simply because the art fails to teach or suggest every element recited in the claim.

With respect to the examiner's reliance upon Staples et al. U.S. Patent No. 5,994,440 ('440), appellants fail to see where hollow microspheres are disclosed in the reference. It is further submitted that if the examiner wishes to rely on the '440 patent, the reference should have been cited in a rejection, rather than an Advisory Action, to allow appellants a reasonable opportunity to refute the examiner's assertions.

In the Advisory Action, the examiner states that substituting one hydrophilic polymer for another "is still *prima facie* obvious". Again, this is a bald, unsupported statement. The range of hydrophilic polymers is great—some water soluble, some not, low molecular weight, high molecular weight, different structures, etc.. All hydrophilic polymers are not

interchangeable, and persons skilled in the art do *not* simply substitute one of a myriad hydrophilic polymers for another. The examiner's conclusion is incorrect.

In the Advisory Action, the examiner also makes an argument that a dendritic polymer of the '062 publication would better disperse the calcium phosphate of the '893 patent. Such reasoning is incorrect. In the present claims, there are no fine calcium phosphate particles to disperse. The calcium phosphate is applied to the water-absorbing polymer particle as a dispersion. Once applied, the calcium phosphate is on surfaces of the hydrogel-forming particle and no longer poses an agglomeration problem. Accordingly, there is no incentive to use the modified dendritic polymer of the '062 publication. Further, if the examiner's reasoning was correct, a person skilled in the art would not utilize an *unmodified* dendritic polymer based on the teachings of the '062 publication.

**X. CONCLUSION**

In view of the foregoing remarks, appellants respectfully request that the Board reverse the final rejection of claims 1-17 and 23-27, and that all pending claims should be allowed.

Dated: March 2, 2011

Respectfully submitted,

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**CLAIMS APPENDIX****Claims Involved in the Appeal of Application Serial No. 10/589,727**

1. (Previously presented) Swellable hydrogel-forming polymer particles comprising (a) hydrogel-forming polymer particles, (b) at least one hydrophilic polymer of dendritic structure, and (c) at least one water-insoluble phosphate, wherein (b) and (c) are present on the surfaces of particles (a).
2. (Previously presented) The polymer particles of claim 1 wherein said hydrophilic polymer of dendritic structure comprises a polyester formed from a polyol and 2,2-dimethylolpropionic acid.
3. (Previously presented) The polymer particles of claim 1 wherein said hydrophilic polymer of dendritic structure comprises a polypropyleneimine, a polyamidoamine, or a polyesteramide.
4. (Previously presented) The polymer particles of claim 1 wherein said water-insoluble phosphate comprises a calcium phosphate.
5. (Previously presented) The polymer particles of claim 1 further comprising a powdery additive, a dusty additive, or a mixture thereof.
6. (Previously presented) The polymer particles of claim 5 wherein said additive comprises a metal salt, a pyrogenic silica, a polysaccharide, a nonionic surfactant, a wax, diatomaceous earth, or mixtures thereof.
7. (Previously presented) The polymer particles of claim 5 wherein said additive is present in the form of hollow microspheres which are from 1 to 1000  $\mu\text{m}$  in diameter and whose wall thickness comprises from 1% to 10% of said diameter.
8. (Previously presented) The polymer particles of claim 1 comprising less than 50 weight ppm of particles less than 10  $\mu\text{m}$  in diameter.
9. (Previously presented) The polymer particles of claim 1 comprising less than 50 weight ppm of particles less than 10  $\mu\text{m}$  in diameter after exposure to a mechanical stress.
10. (Previously presented) The polymer particles of claim 1 wherein not less than 90% by weight of the particles are between 150 and 500  $\mu\text{m}$  in diameter and which are characterized by a CRC of not less than 25 g/g, an AUL or not less than 22 g/g, and an SFC of not less than  $80 \times 10^{-7} \text{ cm}^3 \text{ sg}^{-1}$ .

11. (Previously presented) The polymer particles of claim 1 wherein not less than 90% by weight of the particles are between 100 and 600  $\mu\text{m}$  in diameter and which are characterized by a CRC of not less than 25 g/g, an AUL of not less than 22 g/g, and an SFC of not less than  $60 \times 10^{-7} \text{ cm}^3 \text{ sg}^{-1}$ .

12. (Previously presented) The polymer particles of claim 11 wherein not less than 95% by weight of the particles are between 100 and 600  $\mu\text{m}$  in diameter.

13. (Previously presented) The polymer particles of claim 11 wherein not less than 99% by weight of the particles are between 100 and 600  $\mu\text{m}$  in diameter.

14. (Previously presented) The polymer particles of claim 1 having a CRC of not less than 26 g/g and an AUL of not less than 23 g/g.

15. (Previously presented) The polymer particles of claim 1 having a CRC of not less than 30 g/g and an AUL of not less than 25 g/g.

16. (Previously presented) The polymer particles of claim 1 having an SFC of not less than  $80 \times 10^{-7} \text{ cm}^3 \text{ sg}^{-1}$ .

17. (Previously presented) The polymer particles of claim 1 having an SFC of not less than  $120 \times 10^{-7} \text{ cm}^3 \text{ sg}^{-1}$ .

18. (Cancelled)

19. (Cancelled)

20. (Cancelled)

21. (Cancelled)

22. (Cancelled)

23. (Previously presented) The polymer particles of claim 1 wherein the hydrogel-forming polymer particles (a) comprise a partially neutralized polyacrylic acid.

24. (Previously presented) The polymer particles of claim 1 wherein the particles are surface-postcrosslinked with at least one surface postcrosslinker.

25. (Previously presented) The polymer particles of claim 1 wherein the hydrophilic polymer of dendritic structure is present on the surfaces of particles (a) from 0.005% to 10%, by weight, of the swellable hydrogel-forming polymer particles.



26. (Previously presented) The polymer particles of claim 1 wherein said hydrophilic polymer of dendritic structure comprises a polyester formed from a polyol and 2,2-dimethylolpropionic acid and said water insoluble phosphate comprises a calcium phosphate.

27. (Previously presented) The polymer particles of claim 1 wherein said hydrophilic polymer of dendritic structure comprises a polypropyleneimine, a polyamidoamine, or a polyesteramide and said water insoluble phosphate comprises a calcium phosphate.

**EVIDENCE APPENDIX**

A-5 T. Buchholz et al. eds., *Modern Superabsorbent Polymer Technology*. (1998).  
page 97.

A-8 BOLTORN<sup>®</sup> Technical Bulletin

A-16 Excerpts from Goldmann et al. U.S. Patent No. 5,599,335

A-23 Milco et al. U.S. Patent No. 5,731,095

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# MODERN SUPERABSORBENT POLYMER TECHNOLOGY

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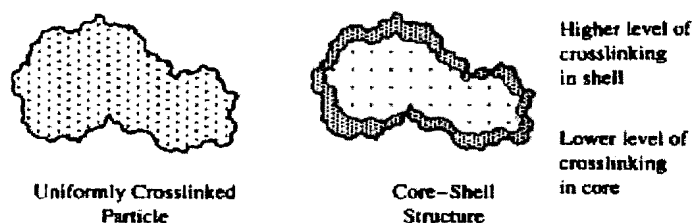
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### 3.2.8. Addition of Post-Treatments

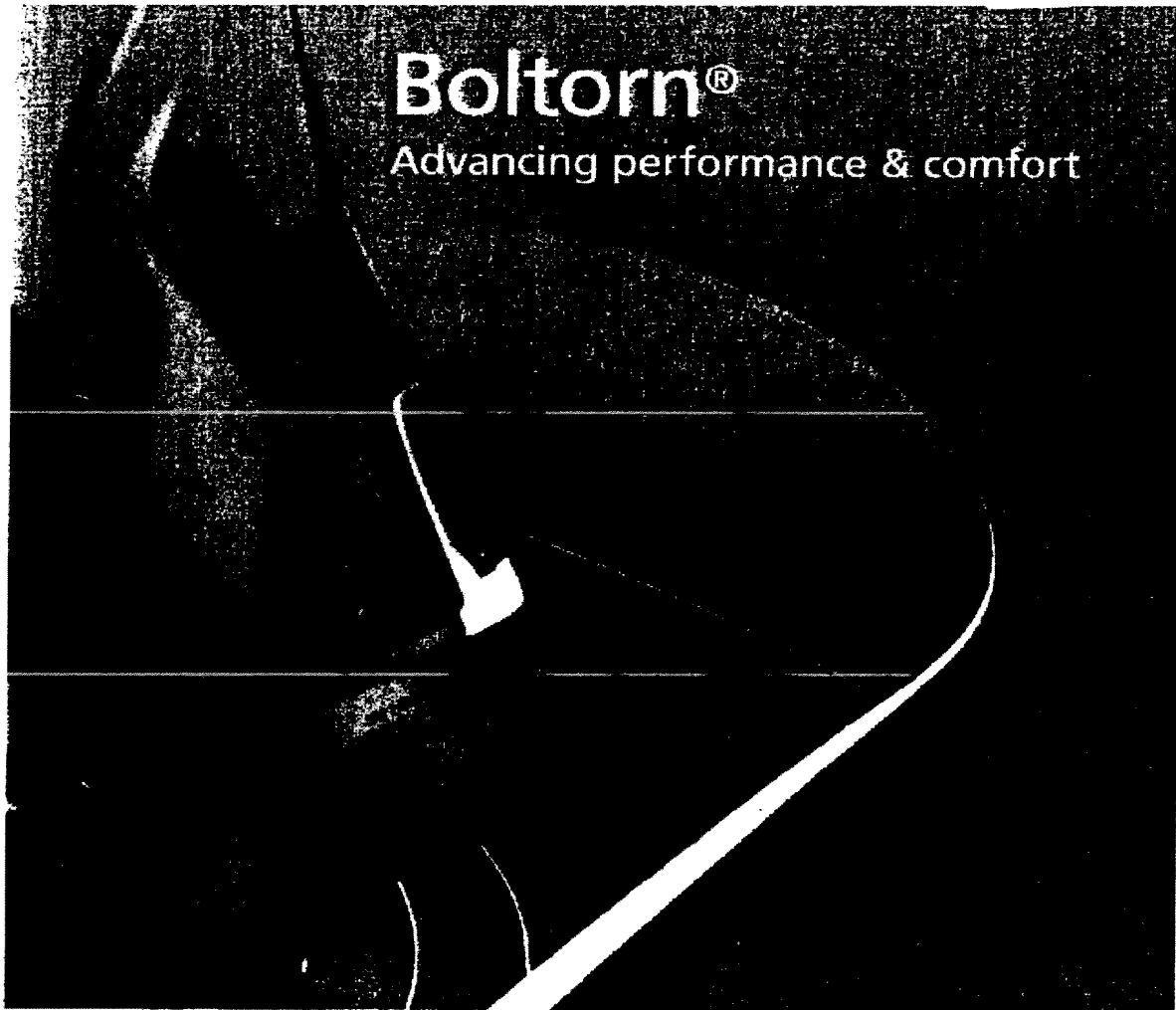
**3.2.8.1. Advanced Products.** The processes described above produce a particle with crosslinking that may be assumed to be essentially uniform throughout the particle. As such, the swelling and modulus behavior of the product particles can be described by theories of network swelling and elasticity (see Chapter 5). One problem associated with these superabsorbent polymers was also recognized in a variety of water soluble polymers, e.g., poly(acrylamide), cellulose ethers,<sup>95</sup> or soluble poly(acrylic acid).<sup>96</sup> This problem is the tendency of the granular polymers to clump, "gel block," or form fish-eyes when aqueous liquids are added to them or they are added to aqueous liquids. The surfaces of the massed particles swell rapidly to form a soft, deformable layer. The resulting particle deformation and interparticle adhesion reduces interparticle porosity and limits the swelling rate of the polymer mass to the diffusion rate of liquid through the partially swollen mass.

The first attempts to solve this problem in highly absorbent anionic polyelectrolytes used multivalent cations to form a crosslinked surface layer that was more rigid than the original core polymer.<sup>97</sup> Subsequently, to give products with improved dispersibility and absorption rate, the surface of crosslinked polyacrylate particles was reacted with a variety of multifunctional organic compounds.<sup>49,50,98,99</sup> This structural improvement is shown schematically in Figure 3.9. Swelling capacity data as a function of particle size readily demonstrate that a shell of real, as opposed to infinitesimal, thickness is formed by surface crosslinking processes. The shell of higher crosslink density provides a more rigid surface layer during swelling and prevents the gel-blocking that would otherwise occur early in the swelling process (Chapter 5). As a result, liquid can flow through the bed of particles to each particle, increasing the effective surface area available for swelling and the apparent swelling rate. The swelling and modulus behavior of structured particles are discussed in Chapter 5.

Because a surface layer is formed on each individual particle, the crosslinking reaction, but not necessarily the reagent addition, must occur after achieving the desired particle size distribution. Any compound that can react with two or more functional groups on the polymer backbone can function as a surface crosslinking reagent. For superabsorbents, this requires reagents that can react with the car-



**Figure 3.9.** Schematic representation of a uniformly crosslinked superabsorbent particle and a structured particle with a surface layer of higher crosslink density.



**Our dendritic polymers**

- Secure exceptional firmness and comfort in flexible polyurethane foam
- Improve the Tg/flexibility ratio of cast polyurethane elastomer products
- Ensure rapid curing, excellent durability and low toxicity in UV curing applications
- Provide reduced VOC and improved performance in architectural coatings



# The elements of success

**You need a partner who can see the big picture when it comes to your products, your processes and your customers.** Our experience and expertise in the special niches of organic chemistry, process technology and application development are at your service, providing you with a complete chain of solutions to enhance quality and profitability at every step.

**Our versatile intermediates, an essential element of your winning formula, are specifically designed to add value and enhance end-product performance.** Your solution to meeting the increasing demands for safer, lighter, more durable and environmentally friendly end-user products, begins here.

## **Innovation in everything we do**

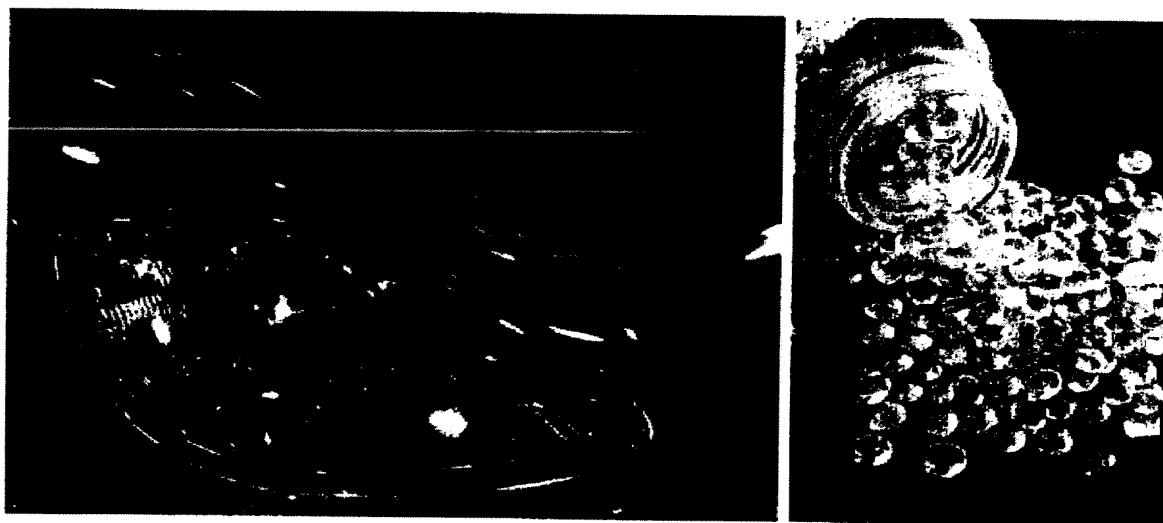
Innovation distinguishes every aspect of our business process. Developing smarter and safer solutions creates real value in new chemical applications. Focused innovation instills leadership and purpose in our business activities, improves internal processes and increases application and product competitiveness.

## **Delivering our promises globally**

Our global presence provides you with reliable solutions and processes, consistent high quality, security of production and supply and delivery with precision. This commitment also means rapid response when product or application support is required and the very best in technical support.

## **Putting the care into chemicals**

We take our responsibilities to heart and are committed to attentive, sustainable business practices. We minimize risks for our customers, our employees and the environment by working proactively to ensure safe products and processes.



## Advancing performance & comfort

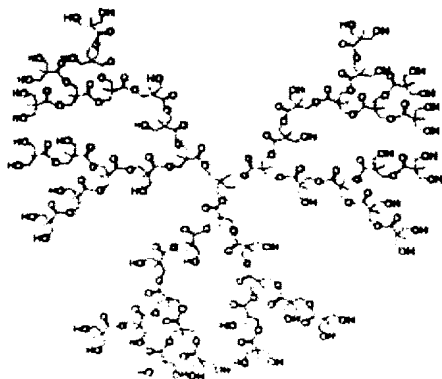
Sharpen your competitive edge by partnering with the global leader in bringing cost-effective dendritic polymers to the market. Dendritic polymers are characterized by a densely branched backbone and a large number of reactive groups. Their globular structures have excellent flow and processing properties at high molecular weight. The exceptional concentration of reactive groups facilitates customization of properties for a wide range of end uses.

The main applications of Boltorn® dendritic polymers:

- ◆ Performance additives for flexible polyurethane foam such as in automotive seating applications.
- ◆ Elastomer cross-linkers to improve the Tg/flexibility ratio of cast polyurethane elastomer products.
- ◆ Oligomer precursors for UV curing applications to achieve very rapid curing and excellent properties.
- ◆ Performance resins for architectural coatings to convert solvent borne resins to waterborne equivalents and reduce the VOC of solvent borne paints.

### Boltorn® technology

- ◆ Large number of primary hydroxyl groups
- ◆ Densely branched polymer backbone
- ◆ Extensive formulation possibilities



### The cutting edge of technology

Our Boltorn® products are produced using polyalcohol cores, hydroxy acids and technology based on caprive materials. The dendritic structures are formed by polymerization of the particular core and 2,2-dimethylol propionic acid (Bis-MPA). The base products obtained are hydroxyl-functional dendritic polyesters. Fully aliphatic and consisting only of tertiary ester bonds, they provide excellent thermal and chemical resistance. Extensive branching also improves reactivity, lowers viscosity and results in balanced mechanical properties. Five base products are available as polymer building blocks and elastomer cross-linkers representing a range in molecular weight, hydroxyl functionality, glass transition temperature (Tg) and polarity.

### Our dendritic base products:

#### Boltorn® H20

16 terminal hydroxyl groups,  
nominal molecular weight of 1,750 g/mol

#### Boltorn® H2003

12 terminal hydroxyl groups,  
nominal molecular weight of 2,300 g/mol

#### Boltorn® H2004

6 terminal hydroxyl groups,  
nominal molecular weight of 3,100 g/mol

#### Boltorn® H30

32 terminal hydroxyl groups,  
nominal molecular weight of 3,600 g/mol

#### Boltorn® H40

64 terminal hydroxyl groups,  
nominal molecular weight of 7,300 g/mol

We welcome your questions. More detailed information and specifications of each product are available on [www.perstorp.com](http://www.perstorp.com) or through your Perstorp sales representative.



# Fine-tuning with polyols

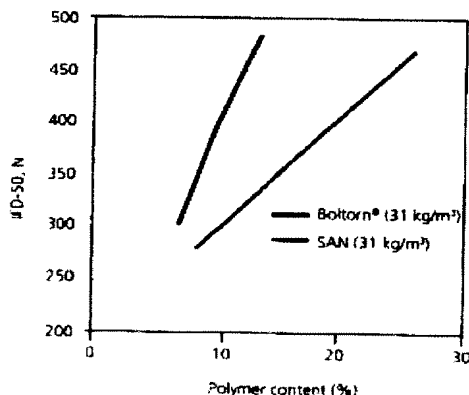
## Boltorn® for polyurethanes

- Millions of car owners already enjoy superior seating comfort with the help of Boltorn® technology. In partnership with a leading automotive foam supplier, we have developed a unique technology that improves the firmness of high-resilience foam articles with dendritic polymer polyols.

### Boltorn® H311 – for exceptional firmness & stability

This liquid polymer polyol provides exceptional compressive load-building characteristics in flexible foam at very low addition levels. It is used as an additive, partially replacing conventional cross-linkers or graft co-polymer polyols of SAN-type. Compared to conventional technology, Boltorn® H311 offers considerable benefits:

- Two to three times the efficiency in providing compressive loads (IFD or CFD) at a given addition solids level, which allows lower average solids levels to be used.
- Exceptional firmness, extending beyond current state-of-the-art technology.
- Improved foam stability due to the cross-linking mechanism and reduced surface voids of finished parts.



Compressive load as function of polymer content for Boltorn® H311 vs. co-polymer polyols

### Boltorn® P500 – new release for high firmness at low compression set

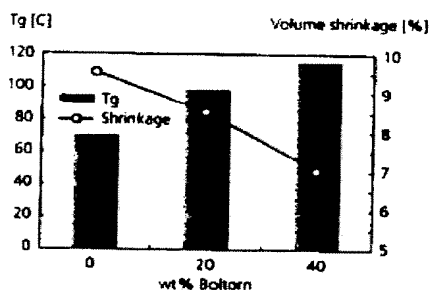
Our newly launched dendritic polymer polyol for molded foam is a liquid water-free product that yields exceptionally low compression set at high firmness when used with graft co-polymer polyols. The low compression set allows you to operate at reduced foam density and still meet the comfort specifications of end users.

Formulation	60-5	60-15	50-11-4
Polyol (Hyperlite 1656), pph	87.95	63.85	63.51
Co-polymer polyol (Hyperlite 1650), pph	12.05	36.15	36.49
Boltorn® P500, pph	0	0	4.19
DEDA-UF, pph	0.50	0.50	1.00
Glycerine, pph	0	0	0
H <sub>2</sub> O, pph	1.76	1.75	2.21
DABCO 33-LV, pph	0.10	0.10	0.36
NIAX A-1, pph	0.08	0.08	0.08
PC77, pph	0.20	0.20	0.00
Y10184, pph	1.00	1.00	0.70
TDI 80, pph	23.61	23.12	33.72
Total wet weight, g	127.25	126.75	142.26
Total dry weight, g	119.60	119.10	130.75
SAN, %	5	15	11
Boltorn® P500, %	0	0	4
Density, kg/m³	60	60	50
IFD-25, N	147	239	192
IFD-65, N	390	633	558
Dry set, %	4	4	2.9

Density reduction at reduced compression set when using Boltorn® P500

### Cross-linkers for increased durability

We offer you two dendritic polyester polyols suitable as cross-linkers for cast polyurethanes and elastomers. Boltorn® H2003 is a polyol of relatively high molecular weight and high hydroxyl value. Added to a polyurethane formulation, it improves the Tg and Shore-hardness of some formulations with aliphatic isocyanates. Boltorn® H2004 is a liquid product with hydrophobic chain stoppers that is used to yield durable systems with high flexibility.



High molecular weight and functionality of acrylated Boltorn® oligomers improves hardness and Tg, yet reduces shrinkage and curl, when replacing polyether in polyether/PEOTA formulation.

## Boltorn® for radiation curing

### Oligomer precursors for superior performance

Boltorn® products enhance radiation curing applications by providing oligomer precursors that significantly increase the average molecular weight of UV formulations at high acrylate concentration. Acrylates based on Boltorn® technology are typically used to partially or fully replace urethane acrylates, other top-end oligomers or acrylates of high functionality. Using Boltorn® dendritic polyols as starters for oligomer acrylates offers significant benefits:

- Excellent reactivity
- Improved scratch resistance and film hardness
- Low shrinkage and good adhesion
- Exceptional flow properties and good pigment wetting
- Improved labeling with low extractables
- Unique molecular weight/viscosity ratio

For coatings, the balance between flow and properties like reactivity, and chemical and scratch resistance, is crucial for meeting end-user demands. Environmental compliance is also a key competitive factor. Radiation curing systems, typically UV, have gained market share in the past decades as very rapid curing and excellent film properties are obtained with low or no VOC emissions.



Acrylated polyol	Di-Penta (DPHA)	Acrylate of Boltorn® P500
Viscosity, mPas, 100% solids, 23°C	14,000	700
Min. UV-dose, tack-free, mJ/cm²	200	200
Erchsen-flex, aluminum, mm	0.4	2.2
Pencil hardness, PC-Sheet, 250µm	3H/4H	2H/3H
Scratch resistance (200 rubs), gloss 60° ref., %	90	91
Tape adhesion on PC-sheet, 0-5, 5 best	2	5
Adhesion, 180° bending test	No	OK

Properties of acrylated Di-Penta and acrylated Boltorn® P500 – all coating formulations cured with 3% Irgacure 500 from Ciba at 12µm film thickness with a UV-dose of 500 mJ/cm² unless otherwise stated

# Designed to enhance

## Boltorn® for architectural coatings

### Boltorn® resins – safer performance

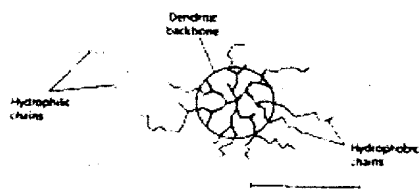
Our Boltorn® performance resins for solvent borne and water-borne architectural coatings help coating formulators comply with environmental demands without compromising coating performance. A number of patented technologies have been developed in which Boltorn® resins improve the performance of architectural coatings. Achieve excellent properties including reduced VOC, improved drying of woodstains and conversion of conventional solvent borne resins to waterborne equivalents.

### Boltorn® U3000 – unique flow properties

For high-solid alkyds, the branched structure of Boltorn® U3000 provides unique flow properties, which allows woodstains and alkyd paints for outdoor applications to comply with recent VOC demands while still securing rapid drying and durability.

### Boltorn® W3000 – efficient & powerful by design

The unique structure of dendritic polymers offers extensive design possibilities. We have developed Boltorn® W3000, a dispersing resin for converting conventional solvent borne alkyd paints into waterborne equivalents. The amphiphilic dendritic structure of Boltorn® W3000 contains both non-ionic water-dispersible and hydrophobic air-drying groups. The result is a powerful high molecular weight surfactant, which also contributes to drying and film properties.



Schematic structure of Boltorn® W3000

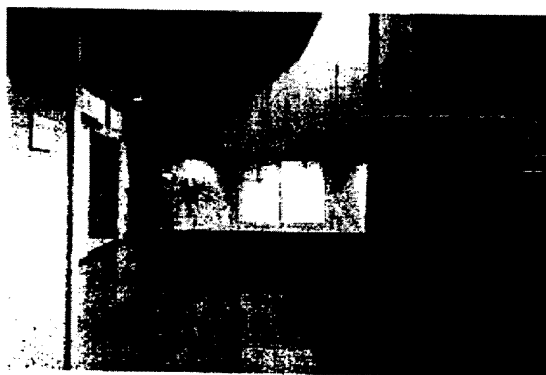
Formulation	Conventional woodstain	Waterborne Boltorn® U3000
Type	oil/alkyd	oil/alkyd/dendritic alkyd
VOC, g/l	595	238
Viscosity, 23°C, mPas	28	72
Drying properties (45µm dry film)		
Film hardness-1 day, Ks	5	45
Film hardness-10 days, Ks	27	35
Film hardness-17 days, Ks	27	33
Film hardness-31 days, Ks	26	33

Effect on VOC and drying properties when adding Boltorn® U3000 to a conventional woodstain available in Scandinavia

High gloss paint for glass application	Boltorn® W3000 stabilized OL 65 alkyd emulsion	Solvent-borne OL 65 alkyd (ref.)	Conventional OL 25 alkyd emulsion
Boltorn® W3000, wt% in paint	2.3	-	-
Alkyd (OL 65), wt% in paint	21.4	34.4	-
Alkyd OL 65-Internally emulsified	-	-	31.8
Solids content, wt%	49	67	51
PVC	17	17	13
VOC, g/l	0	270	0
Gloss, 60°	93	92	95
Drying*			
Dust-free, h	0.5	0.5	0.5
Tack-free, h	4	3	1.5
Through dry, h	5	1.5	15.5
Hard, h	14	5	> 24

\* Beck-Koller, glass panels at 23 °C, 50% humidity, 25 µm DFT

The physical properties of a waterborne paint containing Boltorn® W3000 compared to a solvent borne counterpart and a conventional alkyd emulsion paint





## Your Winning Formula

The Perstorp Group is the world leader in several sectors of the specialty chemicals market. Few chemical companies in the world can rival its 125 years of success. Today we have a rich performance culture distilled from our long history and extensive knowledge in the chemical industry. That culture and knowledge base enables us to produce Winning Formulas for a wide variety of industries and applications.

Our products are used in the aerospace, marine, coatings, chemicals, plastics, engineering and construction industries. They can also be found in automotive, agricultural feed, food, packaging, textile, paper and electronics applications.

Our production plants are strategically located in Europe, North America and Asia and are supplemented by sales offices in all major markets. We can offer you a speedy regional support and a flexible attitude to suit your business needs.

If you want a chemical partner who can offer you focused innovation to enhance your product or application, which is delivered reliably and responsibly look no further. We have a winning formula waiting for you.

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WINNING FORMULAS

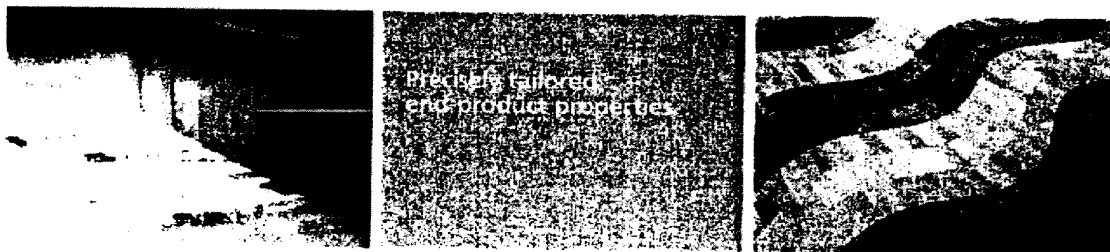
## Product data summary

Product	Soluble in	Appearance	Functionality	OH-value, mg KOH/g	Mw (GPC, g/mol)	T <sub>g</sub> (DMA) °C	Viscosity, Pas (°C)
<b>Polymer building blocks &amp; CASE polyols</b>							
Boltorn® H20	NMP, Diglym Acetone, Glycols	Opaque pellets	16	490 – 520	2,100	25	6 (110)
Boltorn® H2003	EtOH, MEK, Toluene	Transparent	12	280 – 310	2,500	-5	1 (110)
Boltorn® H2004	EtOH, Toluene, Xylene	Yellow liquid	6.4	110 – 130	3,200	-35	15 (23)
Boltorn® H30	MeOH, Acetone, NMP	Opaque pellets	32	490 – 510	3,500	35	40 (110)
Boltorn® H40	MeOH, Acetone, MEK	Transparent pellets	64	470 – 500	5,100	40	80 (110)

Product	Soluble in	Appearance	Water cont. wt %	OH-value, mg KOH/g	Mw (GPC, g/mol)	T <sub>g</sub> (DMA) °C	Viscosity, Pas (°C)
<b>Molded flexible foam</b>							
Boltorn® H311	Polyether/ polyester polyols	Yellow liquid	9.5 – 10.5	235 – 255	5,500	-5	40 (23)
Boltorn® P500	Polyether polyols	Clear liquid	<0.5	560 – 630	1,800	–	12 (23)

Product	Soluble in	Appearance	Functionality	OH-value, mg KOH/g	Mw (GPC, g/mol)	T <sub>g</sub> (DMA) °C	Viscosity, Pas (°C)
<b>Radiation curing</b>							
Boltorn® H20	Acrylic acid + 15% toluene	Opaque pellets	16	490 – 520	2,100	25	6 (110)
Boltorn® H2003	EtOH, MEK, Toluene	Transparent	12	280 – 310	2,500	-5	1 (110)
Boltorn® P500	Acrylic acid + toluene	Clear liquid	hydroxyl	560 – 630	1,800	–	12 (23)
Boltorn® P1000	Acrylic acid + toluene	Clear liquid	hydroxyl	430 – 490	1,500	–	5 (23)

Product	Soluble in	Appearance	Functionality	OH-length % (tri/gly)	Mw (GPC, g/mol)	T <sub>g</sub> (DMA) °C	Viscosity, Pas (°C)
<b>Architectural, waterborne coatings</b>							
Boltorn® U3000	Oils, coalescents, EtOH, Xylene	Yellow liquid	Air-drying	77	6,500	99	1 (23)
Boltorn® W3000	Emulsifying, soluble in alkyds, co-solvents, xylene	Yellow wax	Amphiphilic Air-drying	45 (fully aliphatic)	10,000	99	2.5 (35)



# United States Patent [19]

Goldman et al.

[11] Patent Number: 5,599,335  
[45] Date of Patent: Feb. 4, 1997

[54] **ABSORBENT MEMBERS FOR BODY FLUIDS HAVING GOOD WET INTEGRITY AND RELATIVELY HIGH CONCENTRATIONS OF HYDROGEL-FORMING ABSORBENT POLYMER**

[75] Inventors: Stephen A. Goldman, Wyoming; Nancy A. Haynes, Okcena; Todd L. Mansfield, Cincinnati, all of Ohio; Manfred Pfischke, Steinbach, Germany; Herbert L. Retzsch, Cincinnati, Ohio; Trevor Walker, Cincinnati, Ohio; Gerald A. Young, Cincinnati, Ohio

[73] Assignee: The Procter & Gamble Company, Cincinnati, Ohio

[21] Appl. No.: 219,574

[22] Filed: Mar. 29, 1994

[51] Int. Cl.<sup>6</sup> A61F 13/15; A61F 13/20

[52] U.S. Cl. 604/368; 604/372; 604/378; 604/375

[58] Field of Search 604/358, 367-369, 604/372, 374-376, 378, 381-382, 385.1; 428/327; 325/54.24, 54.26, 54.26, 329.4, 329.5

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Primary Examiner—John G. Weiss

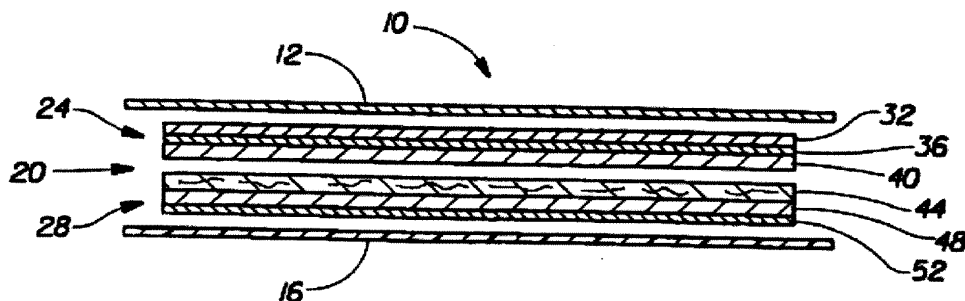
Assistant Examiner—P. Zuttarelli

Attorney, Agent, or Firm—Eric W. Guttag; Carl J. Roof; E. Kelly Linman

## [57] ABSTRACT

Absorbent members useful in the containment of body fluids such as urine, that have at least one region containing hydrogel-forming absorbent polymer in a concentration of from about 60 to 100% by weight and providing a gel-continuous fluid transportation zone when in a swollen state. This hydrogel-forming absorbent polymer has: (a) a Saline Flow Conductivity (SFC) value of at least about  $30 \times 10^{-7}$  cm<sup>3</sup>/sec/g; (b) a Performance under Pressure (PUP) capacity value of at least about 23 g/g under a confining pressure of 0.7 psi (5 kPa); and (c) a basis weight of at least about 10 gsm. In addition, the region where this hydrogel-forming absorbent polymer is present has, even when subjected to normal use conditions, sufficient wet integrity such that the gel-continuous zone substantially maintains its ability to acquire and transport body fluids through the gel-continuous zone.

40 Claims, 10 Drawing Sheets



5,599,335

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instances. However, AUL is inadequate for determining which hydrogel-forming absorbent polymers will provide the absorbency properties necessary so that the concentration of these polymers in absorbent structures can be increased without significant gel blocking or some other undesirable effect. It has been discovered that the permeability or flow conductivity of the hydrogel formed when these absorbent polymers swell in the presence of body fluids is extremely important to feasible inclusion of high concentrations of these absorbent polymers in localized regions or throughout the absorbent member. Differences in permeability or flow conductivity of the absorbent polymer can directly impact on the ability of the resultant hydrogel layer to acquire and distribute body fluids.

Indeed, certain of the hydrogel-forming absorbent polymers disclosed in U.S. Pat. Nos. 5,147,343 and 5,149,335 as having satisfactory AUL values will have inadequate permeability or flow conductivity to be useful at high concentrations in absorbent members. In order to have a high AUL value, it is only necessary that the hydrogel layer formed have at least minimal permeability such that, under a confining pressure of 0.3 psi, gel blocking does not occur to any significant degree. The degree of permeability needed to simply avoid gel blocking is much less than that needed to provide good fluid transportation properties. Hydrogel-forming absorbent polymers that avoid gel blocking can still be greatly deficient in these other fluid handling properties.

The permeability/flow conductivity of these hydrogel-forming absorbent polymers can be defined in terms of their Saline Flow Conductivity (SFC) values. SFC measures the ability of a material to transport saline fluids, such as the ability of the hydrogel layer formed from the swollen hydrogel-forming absorbent polymer to transport body fluids. A good example of a material having relatively high SFC value is an air-laid web of wood-pulp fibers. Typically, an air-laid web of pulp fibers (e.g. having a density of 0.15 g/cc) will exhibit an SFC value of about  $200 \times 10^{-7} \text{ cm}^3/\text{sec/g}$ . By contrast, typical hydrogel-forming absorbent polymers such as Aqualic L-74 (made by Nippon Shokubai Co., LTD) and Nalco-1180 (made by Nalco Chemical Co.) exhibit SFC values of at most  $1 \times 10^{-7} \text{ cm}^3/\text{sec/g}$ . Accordingly, it would be highly desirable to be able to use hydrogel-forming absorbent polymers that more closely approach an air-laid web of wood pulp fibers in terms of SFC. This is particularly true if higher, localized concentrations of these hydrogel-forming absorbent polymers are to be effectively used in the absorbent member. (Higher SFC values also are reflective of the ability of the resultant hydrogel to acquire body fluids under normal usage conditions.)

Another problem with using AUL values measured according to U.S. Pat. Nos. 5,147,343 and 5,149,335 is that they do not reflect all of the potential pressures that can be operative on the hydrogel-forming polymer in the absorbent structure. As noted above, AUL is measured in these patents at a pressure of about 0.3 psi. It is believed that a much higher confining pressure of about 0.7 psi more adequately reflects the full range of localized mechanical pressures (e.g., sitting, sleeping, squatting, taping, elastics, leg motions, other tension and torsional motions) on an absorbent structure. See U.S. Pat. No. 5,147,345 (Young et al), issued Sep. 15, 1992. Additionally, many of the absorbent structures that comprise these hydrogel-forming absorbent polymers can include other components, such as an acquisition layer that receives the initial discharge of body fluids. See, for example, U.S. Pat. No. 4,673,402 (Weisman et al), issued Jun. 16, 1987 and U.S. Pat. No. 4,935,022 (Lash et al), issued Jun. 19, 1990. This acquisition layer can comprise

6

fibers, such as certain chemically stiffened fibers, that have a relatively high capillary suction. See, for example, U.S. Pat. No. 5,217,445 (Young et al), issued Jun. 8, 1993. To take into account these additional capillary pressures that could affect fluid acquisition by these hydrogel-forming absorbent polymers, it is more realistic to measure demand absorbency performance under a higher pressure, i.e., about 0.7 psi. This would take into better account not only the localized mechanical pressures exerted during use, but also the additional capillary pressures resulting from other components (e.g., acquisition layer) present in the absorbent structure.

Another factor that has to be considered in order to take full advantage of the permeability/flow conductivity of the hydrogel layer formed from these absorbent polymers is the wet integrity of the region or regions in the absorbent member that comprise these polymers. For hydrogel-forming absorbent polymers having relatively high SFC values, it is extremely important that the region(s) in which polymers are present have good wet integrity. By "good wet integrity" is meant that the region or regions in the absorbent member having the high concentration of hydrogel-forming absorbent polymer have sufficient integrity in a dry, partially wet, and/or wetted state such that the physical continuity (and thus the capability of acquiring and transporting fluid through contiguous interstitial voids/capillaries) of the hydrogel formed upon swelling in the presence of body fluids is not substantially disrupted or altered, even when subjected to normal use conditions. During normal use, absorbent cores in absorbent articles are typically subjected to tensional and torsional forces of varying intensity and direction. These tensional and torsional forces include bunching in the crotch area, stretching and twisting forces as the person wearing the absorbent article walks, squats, bends, and the like. If wet integrity is inadequate, these tensional and torsional forces can potentially cause a substantial alteration and/or disruption in the physical continuity of the hydrogel such that its capability of transporting fluids through the contiguous voids and capillaries is degraded, e.g., the hydrogel layer can be partially separated, fully separated, have gaps introduced, have areas that are significantly thinned, and/or broken up into a plurality of significantly smaller segments. Such alteration could minimize or completely negate any advantageous permeability/flow conductivity properties of the hydrogel-forming absorbent polymer.

Accordingly, it would be desirable to be able to provide an absorbent member comprising: (1) a region or regions having a relatively high concentration of hydrogel-forming absorbent polymer; (2) with permeability/flow conductivity properties more like an air-laid fibrous web; (3) that can readily acquire fluids from even high capillary suction acquisition layers under typical usage pressures; (4) in a matrix that provides sufficient wet integrity such that its capability for acquiring and transporting fluids is not substantially reduced or minimized, even when subjected to normal use forces.

#### DISCLOSURE OF THE INVENTION

The present invention relates to absorbent members useful in the containment of body fluids such as urine. These absorbent members comprise at least one region having hydrogel-forming absorbent polymer in a concentration of from about 60 to 100% by weight and providing a gel-continuous fluid transportation zone when in a swollen state. This hydrogel-forming absorbent polymer has:

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degradation in other hydrogel-forming absorbent polymer properties such as Performance Under Pressure (PUP) capacity and level of extractable polymer. Thus, for example, it can be useful to use a size cut having a mass median size in the range of from about 500 to about 710 microns wherein only minimal mass fractions of the particulates have sizes either greater than about 710 microns or less than about 500 microns. Alternatively, a broader size cut wherein the particles generally have a size in the range of from about 300 microns to about 800 microns can be useful.

#### b. Physical Properties

##### (1). Saline Flow Conductivity (SPC)

An important characteristic of the hydrogel-forming absorbent polymers useful in the present invention is their permeability or flow conductivity when swollen with body fluids so as to form a hydrogel zone or layer. This permeability or flow conductivity is defined herein in terms of the Saline Flow Conductivity (SPC) value of the hydrogel-forming absorbent polymer. SFC measures the ability of the formed hydrogel zone or layer to transport or distribute body fluids under usage pressures. It is believed that when a hydrogel-forming absorbent polymer is present at high concentrations in an absorbent member and then swells to form a hydrogel under usage pressures, the boundaries of the hydrogel come into contact, and interstitial voids in this high-concentration region become generally bounded by hydrogel. When this occurs, it is believed the permeability or flow conductivity properties of this region are generally reflective of the permeability or flow conductivity properties of a hydrogel zone or layer formed from the hydrogel-forming absorbent polymer alone. It is further believed that increasing the permeability of these swollen high-concentration regions to levels that approach or even exceed conventional acquisition/distribution materials, such as wood-pulp fluff, can provide superior fluid handling properties for the absorbent member and absorbent core, thus decreasing incidents of leakage, especially at high fluid loadings. (Higher SFC values also are reflective of the ability of the formed hydrogel to acquire body fluids under normal usage conditions.)

The SFC value of the hydrogel-forming absorbent polymers useful in the present invention is at least about  $30 \times 10^{-7}$  cm<sup>3</sup>/sec/g, preferably at least about  $50 \times 10^{-7}$  cm<sup>3</sup>/sec/g, and most preferably at least about  $100 \times 10^{-7}$  cm<sup>3</sup>/sec/g. Typically, these SFC values are in the range of from about 30 to about  $1000 \times 10^{-7}$  cm<sup>3</sup>/sec/g, more typically from about 50 to about  $500 \times 10^{-7}$  cm<sup>3</sup>/sec/g, and most typically from about 100 to about  $350 \times 10^{-7}$  cm<sup>3</sup>/sec/g. A method for determining the SFC value of these hydrogel-forming absorbent polymers is provided hereafter in the Test Method Section.

##### (2). Performance Under Pressure (PUP)

Another important characteristic of the hydrogel-forming absorbent polymers useful in the present invention is their demand absorbency capacity under a high confining pressure. This demand absorbency capacity is defined in terms of the polymer's Performance Under Pressure (PUP) capacity. PUP capacity measures the ability of a high basis weight zone or layer of the hydrogel-forming absorbent polymer to absorb body fluids under usage pressures. When a hydrogel-forming absorbent polymer is incorporated into an absorbent member at high concentrations, the polymer needs to be capable of absorbing large quantities of body fluids in a

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reasonable time period under usage pressures. Otherwise, the absorbent member will be less effective at absorbing fluid, e.g., by partitioning fluid from acquisition components that provide temporary holding capacity for this fluid. When this occurs, it is believed that the absorbent core is left with insufficient temporary holding capacity to contain subsequent gushes of body fluid and can leak prematurely. Also, to be able to deliver a high storage capacity from an absorbent core of minimal weight and thickness, the hydrogel-forming absorbent polymer needs to have a relatively high PUP capacity. A relatively high PUP capacity hydrogel-forming polymer is also needed to provide economical absorbent cores.

Usage pressures exerted on the hydrogel-forming absorbent polymer include both mechanical pressures (e.g., exerted by the weight and motions of the user, taping forces, etc.) and capillary pressures (e.g., resulting from the acquisition component(s) in the absorbent core that temporarily hold fluid before it is absorbed by the hydrogel-forming absorbent polymer.) It is believed that a total pressure of about 0.7 psi (5 kPa) is reflective of the sum of these pressures on the hydrogel-forming absorbent polymer as it absorbs body fluids under usage conditions.

The PUP capacity of hydrogel-forming absorbent polymers useful in the present invention is generally at least about 23 g/g, preferably at least about 25 g/g, and most preferably at least about 29 g/g. Typically, these PUP capacity values are in the range of from about 23 to about 35 g/g, more typically from about 25 to about 33 g/g, and most typically from about 29 to about 33 g/g. A method for determining the PUP capacity value of these hydrogel-forming absorbent polymers is provided hereafter in the Test Method Section.

##### (3). Extractable Polymer

Another important characteristic of hydrogel-forming absorbent polymers useful in the present invention is the level of extractable polymer material present therein. See U.S. Pat. No. 4,654,039 (Brandt et al), issued Mar. 31, 1987 (reissued Apr. 19, 1988 as Re. 32,649). Many hydrogel-forming absorbent polymers contain significant levels of extractable polymer material. This extractable polymer material can be leached out from the resultant hydrogel by body fluids (e.g., urine) during the time period such body fluids remain in contact with the hydrogel-forming absorbent polymer. It is believed such extracted polymer material can alter both the chemical characteristics (e.g., osmolality) and physical characteristics (e.g., viscosity) of the body fluid to such an extent that the fluid is more slowly absorbed and more poorly held by the hydrogel. This polymer contaminated fluid is also more poorly transported through the absorbent member. Such a situation can contribute to undesirable and premature leakage of body fluid from the absorbent article. Thus it is desirable to use hydrogel-forming absorbent polymers with lower levels of extractable polymer material.

The importance of not adversely impacting the effective absorption/retention of body fluids by the swollen hydrogel-forming absorbent polymer, or the facile transport of body fluids through regions of the absorbent member containing the swollen polymer, is believed to be particularly true as: (a) the quantity of polymer in the absorbent member is increased; (b) the quantities of other absorbent components (e.g., fibers) are decreased; and/or (c) the localized concentration of polymer in the absorbent member is increased.



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backsheet are joined directly to each other at the periphery thereof. The topsheet and backsheet can also be indirectly joined together by directly joining them to the absorbent core by the attachment means.

The backsheet is typically impervious to body fluids and is preferably manufactured from a thin plastic film, although other flexible fluid impervious materials may also be used. As used herein, the term "flexible" refers to materials that are compliant and will readily conform to the general shape and contours of the human body. The backsheet prevents body fluids absorbed and contained in the absorbent core from wetting articles that contact the such as pants, pajamas, undergarments, and the like. The backsheet can comprise a woven or nonwoven material, polymeric films such as thermoplastic films of polyethylene or polypropylene, or composite materials such as a film-coated nonwoven material. Preferably, the backsheet is a polyethylene film having a thickness of from about 0.012 mm (0.5 mil) to about 0.051 mm (2.0 mils). Exemplary polyethylene films are manufactured by Clopay Corporation of Cincinnati, Ohio, under the designation P 18-0401 and by Ethyl Corporation, Visqueen Division, of Terre Haute, Ind., under the designation XP-39385. The backsheet is preferably embossed and/or matte finished to provide a more clothlike appearance. Further, the backsheet can permit vapors to escape from the absorbent core (i.e., breathable) while still preventing body fluids from passing through the backsheet.

The topsheet is compliant, soft feeling, and non-irritating to the wearer's skin. Further, the topsheet is fluid pervious permitting body fluids to readily penetrate through its thickness. A suitable topsheet can be manufactured from a wide range of materials such as woven and nonwoven materials; polymeric materials such as apertured formed thermoplastic films, apertured plastic films, and hydroformed thermoplastic films; porous foams; reticulated foams; reticulated thermoplastic films; and thermoplastic scrim. Suitable woven and nonwoven materials can be comprised of natural fibers (e.g., wood or cotton fibers), synthetic fibers (e.g., polymeric fibers such as polyester, polypropylene, or polyethylene fibers) or from a combination of natural and synthetic fibers.

Preferred topsheets for use in absorbent articles of the present invention are selected from high loft nonwoven topsheets and aperture formed film topsheets. Aperture formed films are especially preferred for the topsheet because they are pervious to body fluids and yet non-absorbent and have a reduced tendency to allow fluids to pass back through and rewet the wearer's skin. Thus, the surface of the formed film that is in contact with the body remains dry, thereby reducing body soiling and creating a more comfortable feel for the wearer. Suitable formed films are described in U.S. Pat. No. 3,929,135 (Thompson), issued Dec. 30, 1975; U.S. Pat. No. 4,324,246 (Mullane, et al.), issued Apr. 13, 1982; U.S. Pat. No. 4,342,314 (Radel, et al.), issued Aug. 3, 1982; U.S. Pat. No. 4,463,045 (Ahr et al.), issued Jul. 31, 1984; and U.S. Pat. No. 5,006,394 (Baird), issued Apr. 9, 1991. Each of these patents are incorporated herein by reference. Particularly preferred microapertured formed film topsheets are disclosed in U.S. Pat. No. 4,609,518 (Curro et al), issue Sep. 2, 1986 and U.S. Pat. No. 4,629,643 (Curro et al), issued Dec. 16, 1986, which are incorporated by reference. The preferred topsheet for use in catamenial products of the present invention is the formed film described in one or more of the above patents and marketed on sanitary napkins by The Procter & Gamble Company of Cincinnati, Ohio as "DRI-WEAVE®."

The body surface of the formed film topsheet can be hydrophilic so as to help body fluids to transfer through the

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topsheet faster than if the body surface was not hydrophilic so as to diminish the likelihood that fluid will flow off the topsheet rather than flowing into and being absorbed by the absorbent structure. In a preferred embodiment, surfactant is incorporated into the polymeric materials of the formed film topsheet such as is described in U.S. patent application Ser. No. 07/794,745, "Absorbent Article Having A Nonwoven and Apertured Film Coversheet" filed on Nov. 19, 1991 by Aziz, et al., which is incorporated by reference. Alternatively, the body surface of the topsheet can be made hydrophilic by treating it with a surfactant such as is described in the above referenced U.S. Pat. No. 4,950,254, incorporated herein by reference.

F. Test Methods

### 1. Saline Flow Conductivity (SFC)

This test determines the Saline Flow Conductivity (SFC) of the gel layer formed from hydrogel-forming absorbent polymer that is swollen in Jayco synthetic urine under a confining pressure. The objective of this test is to assess the ability of the hydrogel layer formed from a hydrogel-forming absorbent polymer to acquire and distribute body fluids when the polymer is present at high concentrations in an absorbent member and exposed to usage mechanical pressures. Darcy's law and steady-state flow methods are used for determining saline flow conductivity. (See, for example, "Absorbency," ed. by P. K. Chatterjee, Elsevier, 1985, Pages 42-43 and "Chemical Engineering Vol. II, Third Edition, J. M. Coulson and J. F. Richardson, Pergamon Press, 1978, Pages 125-127.)

The hydrogel layer used for SFC measurements is formed by swelling a hydrogel-forming absorbent polymer in Jayco synthetic urine for a time period of 60 minutes. The hydrogel layer is formed and its flow conductivity measured under a mechanical confining pressure of 0.3 psi (about 2 kPa). Flow conductivity is measured using a 0.118M NaCl solution. For a hydrogel-forming absorbent polymer whose uptake of Jayco synthetic urine versus time has substantially leveled off, this concentration of NaCl has been found to maintain the thickness of the hydrogel layer substantially constant during the measurement. For some hydrogel-forming absorbent polymers, small changes in hydrogel-layer thickness can occur as a result of polymer swelling, polymer deswelling, and/or changes in hydrogel-layer porosity. A constant hydrostatic pressure of 4920 dyne/cm<sup>2</sup> (5 cm of 0.118M NaCl) is used for the measurement.

Flow rate is determined by measuring the quantity of solution flowing through the hydrogel layer as a function of time. Flow rate can vary over the duration of the measurement. Reasons for flow-rate variation include changes in the thickness of the hydrogel layer and changes in the viscosity of interstitial fluid, as the fluid initially present in interstitial voids (which, for example, can contain dissolved extractable polymer) is replaced with NaCl solution. If flow rate is time dependent, then the initial flow rate, typically obtained by extrapolating the measured flow rates to zero time, is used to calculate flow conductivity. The saline flow conductivity is calculated from the initial flow rate, dimensions of the hydrogel layer, and hydrostatic pressure. For systems where the flow rate is substantially constant, a hydrogel-layer permeability coefficient can be calculated from the saline flow conductivity and the viscosity of the NaCl solution.

A suitable apparatus 610 for this test is shown in FIG. 7. This apparatus includes a constant hydrostatic head reservoir indicated generally as 612 that sits on a laboratory jack

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indicated generally as 614. Reservoir 612 has lid 616 with a stoppered vent indicated by 618 so that additional fluid can be added to reservoir 612. An open-ended tube 620 is inserted through lid 616 to allow air to enter reservoir 612 for the purpose of delivering fluid at a constant hydrostatic pressure. The bottom end of tube 620 is positioned so as to maintain fluid in cylinder 634 at a height of 5.0 cm above the bottom of hydrogel layer 668 (see FIG. 8).

Reservoir 612 is provided with a generally L-shaped delivery tube 622 having an inlet 622a that is below the surface of the fluid in the reservoir. The delivery of fluid by tube 622 is controlled by stopcock 626. Tube 622 delivers fluid from reservoir 612 to a piston/cylinder assembly generally indicated as 628. Beneath assembly 628 is a support screen (not shown) and a collection reservoir 630 that sits on a laboratory balance 632.

Referring to FIG. 7, assembly 628 basically consists of a cylinder 634, a piston generally indicated as 636 and a cover 637 provided with holes for piston 636 and delivery tube 622. As shown in FIG. 7, the outlet 622b of tube 622 is positioned below the bottom end of tube 620 and thus will also be below the surface of the fluid (not shown) in cylinder 634. As shown in FIG. 8, piston 636 consists of a generally cylindrical LEXAN® shaft 638 having a concentric cylindrical hole 640 bored down the longitudinal axis of the shaft. Both ends of shaft 638 are machined to provide ends 642 and 646. A weight indicated as 648 rests on end 642 and has a cylindrical hole 648a bored through the center thereof.

Inserted on the other end 646 is a generally circular Teflon piston head 650 having an annular recess 652 in the bottom thereof. Piston head 650 is sized so as to slidably move inside cylinder 634. As particularly shown in FIG. 9, piston head 650 is provided with four concentric rings of twenty-four cylindrical holes each indicated generally as 654, 656, 658, and 660. As can be seen in FIG. 9, concentric rings 654 to 660 fit within the area defined by recess 652. The holes in each of these concentric rings are bored from the top to bottom of piston head 650. The holes in each ring are spaced by approximately 15 degrees and offset by approximately 7.5 degrees from the holes in adjacent rings. The holes in each ring have a progressively smaller diameter going inwardly from ring 654 (0.204 inch diameter) to ring 660 (0.111 inch diameter). Piston head 650 also has cylindrical hole 662 bored in the center thereof to receive end 646 of shaft 638.

As shown in FIG. 8, a fritted circular glass disc 664 fits within recess 652. Attached to bottom end of cylinder 634 is a No. 400 mesh stainless steel cloth screen 666 that is biaxially stretched to tautness prior to attachment. The sample of hydrogel-forming absorbent polymer indicated as 668 is supported on screen 666.

Cylinder 634 is bored from a transparent LEXAN® rod or equivalent and has an inner diameter of 6.00 cm (area=28.27 cm<sup>2</sup>), a wall thickness of approximately 0.5 cm, and a height of approximately 6.0 cm. Piston head 650 is machined from a solid Teflon rod. It has a height of 0.625 inches and a diameter that is slightly less than the inner diameter of cylinder 634, so that it fits within the cylinder with minimum wall clearances, but still slides freely. Recess 652 is approximately 56 mm in diameter by 4 mm deep. Hole 662 in the center of the piston head 650 has a threaded 0.625 inch opening (18 threads/inch) for end 646 of shaft 638. Fritted disc 664 is chosen for high permeability (e.g., Chemglass Cat No. CG-201-40, 60 mm diameter; X-Coarse Porosity) and is ground so that it fits snugly within recess 652 of piston head 650, with the bottom of the disc being flush with the

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bottom of the piston head. Shaft 638 is machined from a LEXAN® rod and has an outer diameter of 0.875 inches and an inner diameter of 0.250 inches. End 646 is approximately 0.5 inches long and is threaded to match hole 662 in piston head 650. End 642 is approximately an inch long and 0.623 inches in diameter, forming an annular shoulder to support the stainless steel weight 648. Fluid passing through the hole 640 in shaft 638 can directly access the fritted disc 664. The annular stainless steel weight 648 has an inner diameter of 0.625 inches, so that it slips onto end 642 of shaft 638 and rests on the annular shoulder formed therein. The combined weight of fritted glass disc 664, piston 636 and weight 648 equals 596 g, which corresponds to a pressure of 0.3 psi for an area of 28.27 cm<sup>2</sup>. Cover 637 is machined from LEXAN® or its equivalent and is dimensioned to cover the top of cylinder 634. It has an 0.877 inch opening in the center thereof for shaft 638 of piston 636 and a second opening near the edge thereof for delivery tube 622.

The cylinder 634 rests on a 16 mesh rigid stainless steel support screen (not shown) or equivalent. This support screen is sufficiently permeable so as to not impede fluid flow into the collection reservoir 630. The support screen is generally used to support cylinder 634 when the flow rate of saline solution through assembly 628 is greater than about 0.02 g/sec. For flow rates less than about 0.02 g/sec, it is preferable that there be a continuous fluid path between cylinder 634 and the collection reservoir. This can be accomplished by replacing the support screen, collection reservoir 630, and analytical balance 632 with analytical balance 716, reservoir 712, fritted funnel 718, and the respective connecting tubes and valves of apparatus 710 (see FIG. 10), and positioning cylinder 634 on the fritted disc in fritted funnel 718.

Jayco synthetic urine used in this method is prepared by dissolving a mixture of 2.0 g KCl, 2.0 g Na<sub>2</sub>SO<sub>4</sub>, 0.85 g NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, 0.15 g (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, 0.19 g CaCl<sub>2</sub>, and 0.23 g MgCl<sub>2</sub> to 1.0 liter with distilled water. The salt mixture can be purchased from Endovations, Reading, Pa. (cat No. JA-00131-000-01).

The 0.118M NaCl solution is prepared by dissolving 6.896 g NaCl (Baker Analyzed Reagent or equivalent) to 1.0 liters with distilled water.

An analytical balance 632 accurate to 0.01 g (e.g., Mettler PM4000 or equivalent) is typically used to measure the quantity of fluid flowing through the hydrogel layer 668 when the flow rate is about 0.02 g/sec or greater. A more accurate balance (e.g., Mettler AE200 or equivalent) can be needed for less permeable hydrogel layers having lower flow rates. The balance is preferably interfaced to a computer for monitoring fluid quantity versus time.

The thickness of hydrogel layer 668 in cylinder 634 is measured to an accuracy of about 0.1 mm. Any method having the requisite accuracy can be used, as long as the weights are not removed and the hydrogel layer is not additionally compressed or disturbed during the measurement. Using a caliper gauge (e.g., Manostat 15-100-500 or equivalent) to measure the vertical distance between the bottom of the stainless steel weight 648 and the top of cover 637, relative to this distance with no hydrogel layer 668 in cylinder 634 is acceptable. Also acceptable is the use of a depth gauge (e.g., Ono Sokki BG-225 or equivalent) to measure the position of piston 636 or stainless steel weight 648 relative to any fixed surface, compared to its position with no hydrogel layer in cylinder 634.

The SPC measurement is performed at ambient temperature (i.e., 20°-25° C.) and is carried out as follows:

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0.9 gm aliquot of hydrogel-forming absorbent polymer (corresponding to a basis weight of 0.032 gm/cm<sup>2</sup>) is added to cylinder 634 and distributed evenly on screen 666. For most hydrogel-forming absorbent polymers, moisture content is typically less than 5%. For these, the quantity of hydrogel-forming absorbent polymer to be added can be determined on a wet-weight (as is) basis. For hydrogel-forming absorbent polymers having a moisture content greater than about 5%, the added polymer weight should be corrected for moisture (i.e., the added polymer should be 0.9 g on a dry-weight basis). Care is taken to prevent hydrogel-forming absorbent polymer from adhering to the cylinder walls. Piston 636 (minus weight 648) with disc 664 positioned in recess 652 of piston head 650 is inserted into cylinder 634 and positioned on top of the dry hydrogel-forming absorbent polymer 668. If necessary, piston 636 can be turned gently to more-uniformly distribute the hydrogel-forming absorbent polymer on screen 666. Cylinder 634 is then covered with cover 637 and weight 648 is then positioned on end 642 of shaft 638.

A fritted disc (coarse or extra coarse) having a diameter greater than that of cylinder 634 is positioned in a wide/shallow flat-bottomed container that is filled to the top of the fritted disc with Jayco synthetic urine. The piston/cylinder assembly 628 is then positioned on top of this fritted glass disc. Fluid from the container passes through the fritted disc and is absorbed by the hydrogel-forming absorbent polymer 668. As the polymer absorbs fluid, a hydrogel layer is formed in cylinder 634. After a time period of 60 minutes, the thickness of the hydrogel layer is determined. Care is taken that the hydrogel layer does not lose fluid or take in air during this procedure.

The piston/cylinder assembly 628 is then transferred to apparatus 610. The support screen (not shown) and any gap between it and the piston/cylinder assembly 628 is pre-saturated with saline solution. If the fritted funnel 718 of the PUP apparatus 710 is used to support cylinder 634, the surface of the fritted funnel should be minimally elevated relative to the height of the fluid in the collection reservoir, with valves between the fritted funnel and the collection reservoir being in the open position. (The fritted funnel elevation should be sufficient such that fluid passing through the hydrogel layer does not accumulate in the funnel.)

The SFC measurement is initiated by adding NaCl solution through hole 640 in shaft 638 in order to expel air from piston head 650 and then turning stopcock 626 to an open position so that delivery tube 622 delivers fluid to cylinder 634 to a height of 5.0 cm above the bottom of hydrogel layer 668. Although the measurement is considered to have been initiated ( $t_0$ ) at the time NaCl solution is first added, the time at which a stable hydrostatic pressure, corresponding to 5.0 cm of saline solution, and a stable flow rate is attained ( $t_1$ ) is noted. (The time  $t_1$  should typically be about one minute or less.) The quantity of fluid passing through hydrogel layer 668 versus time is determined gravimetrically for a time period of 10 minutes. After the elapsed time, piston/cylinder assembly 628 is removed and the thickness of hydrogel layer 668 is measured. Generally the change in thickness of the hydrogel layer is less than about 10%.

In general, flow rate need not be constant. The time-dependent flow rate through the system,  $F_p(t)$  is determined, in units of g/sec, by dividing the incremental weight of fluid passing through the system (in grams) by incremental time (in seconds). Only data collected for times between  $t_1$  and 10 minutes is used for flow rate calculations. Flow rate results between  $t_1$  and 10 minutes is used to calculate a value for  $F_p(t=0)$ , the initial flow rate through the hydrogel layer.

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$F_p(t=0)$  is calculated by extrapolating the results of a least-squares fit of  $F_p(t)$  versus time to  $t=0$ .

For a layer having a very high permeability (e.g., a flow rate greater than -2 g/sec), it may not be practical to collect fluid for the full 10 minute time period. For flow rates greater than -2 g/sec, the time of collection can be shortened in proportion to the flow rate.

For some hydrogel-forming absorbent polymers having extremely low permeability, absorption of fluid by the hydrogel competes with transport of fluid through the hydrogel layer and either there is no flow of fluid through the hydrogel layer and into the reservoir or, possibly, there is a net absorption of fluid out of the PUP reservoir. For these extremely low permeability hydrogel layers, it is optional to extend the time for Jayco SynUrine absorption to longer periods (e.g., 16 hours).

In a separate measurement, the flow rate through apparatus 610 and the piston/cylinder assembly 628 ( $F_p$ ) is measured as described above, except that no hydrogel layer is present. If  $F_p$  is much greater than the flow rate through the system when the hydrogel layer is present,  $F_p$ , then no correction for the flow resistance of the SFC apparatus and the piston/cylinder assembly is necessary. In this limit,  $F_p = F_p$ , where  $F_p$  is the contribution of the hydrogel layer to the flow rate of the system. However if this requirement is not satisfied, then the following correction is used to calculate the value of  $F_p$  from the values of  $F_p$  and  $F_p$ :

$$F_p = (F_p - F_p) / (F_p - F_p)$$

The Saline Flow Conductivity (K) of the hydrogel layer is calculated using the following equation:

$$K = (F_p(t=0) - I_0) / (\rho \times A \times \Delta P)$$

where  $F_p(t=0)$  is the flow rate in g/sec determined from regression analysis of the flow rate results and any correction due to assembly/apparatus flow resistance,  $I_0$  is the initial thickness of the hydrogel layer in cm,  $\rho$  is the density of the NaCl solution in gm/cm<sup>3</sup>,  $A$  is the area of the hydrogel layer in cm<sup>2</sup>,  $\Delta P$  is the hydrostatic pressure in dyne/cm<sup>2</sup>, and the saline flow conductivity,  $K$ , is in units of cm<sup>3</sup>sec/gm.

The average of three determinations should be reported. For hydrogel layers where the flow rate is substantially constant, a permeability coefficient ( $\kappa$ ) can be calculated from the saline flow conductivity using the following equation:

$$\kappa = K / \eta$$

where  $\eta$  is the viscosity of the NaCl solution in poise and the permeability coefficient,  $\kappa$ , is in units of cm<sup>2</sup>.

The following is an example of how SFC is calculated according to the present invention:

The measured value of  $F_p$  is 412 g/min = 6.87 g/sec. For a single determination on the particulate hydrogel-forming polymer sample 3-5 (Example 3), the extrapolated value for  $F_p(t=0)$  is 33.9 g/min = 0.565 g/sec, with a very-low ratio of slope:intercept of  $9 \times 10^{-2} \text{ sec}^{-1}$ . Correcting for apparatus resistance:

$$F_p = (6.87 - 0.565) / (0.565 - 0.565) = 0.616 \text{ g/sec}$$

Given a 0.118M saline density of 1.003 g/cm<sup>3</sup> (CRC Handbook of Chemistry and Physics, 61st Edition) a hydrogel-layer thickness of 1.134 cm, a hydrogel layer area of 28.27 cm<sup>2</sup>, and a hydrostatic pressure of 4920 dyne/cm<sup>2</sup>.

$$K = (0.616 \times 1.134) / (1.003 \times 28.27 \times 4920) = 5.0 \times 10^{-6} \text{ cm}^3 \text{sec/gm}$$

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Considering the substantially constant flow rate and given a 0.118M saline viscosity of 0.01015 poise (CRC Handbook of Chemistry and Physics, 61st Edition):

$$c = (1.0 \times 10^{-4}) \times 0.01015 = 1.1 \times 10^{-6} \text{ cm}^2$$

## 2. Performance Under Pressure (PUP) Capacity

This test determines the 60 minute gram/gram absorption of synthetic urine for a hydrogel-forming absorbent polymer that is laterally confined in a piston/cylinder assembly under a confining pressure of 0.7 psi (about 5 kPa). The objective of the test is to assess the ability of a hydrogel-forming absorbent polymer layer to absorb body fluids, over a practical period of time, when the polymer is present at high basis weight and high concentrations in an absorbent member and exposed to usage pressures. Usage pressures against which a hydrogel-forming polymer is forced to absorb urine against include mechanical pressures resulting from the weight and/or motions of the wearer, mechanical pressures resulting from elastics and fastening systems, and the hydrostatic suction resulting from adjacent capillary (e.g., fibrous) layers and/or structures as they are drained of fluid.

The test fluid for the PUP capacity test is Jayco synthetic urine. This fluid is absorbed by the hydrogel-forming absorbent polymer under demand absorption conditions at near-zero hydrostatic pressure.

A suitable apparatus 710 for this test is shown in FIG. 10. At one end of this apparatus is a fluid reservoir 712 (such as a petri dish) having a cover 714. Reservoir 712 rests on an analytical balance indicated generally as 716. The other end of apparatus 710 is a fritted funnel indicated generally as 718, a piston/cylinder assembly indicated generally as 720 that fits inside funnel 718, and cylindrical plastic fritted funnel cover indicated generally as 722 that fits over funnel 718 and is open at the bottom and closed at the top, the top having a pinhole. Apparatus 710 has a system for conveying fluid in either direction that consists of sections glass capillary tubing indicated as 724 and 731a, flexible plastic tubing (e.g., 1/4 inch I.D. and 1/4 inch O.D. Tygon tubing) indicated as 731b, stopcock assemblies 726 and 738 and Teflon connectors 748, 750 and 752 to connect glass tubing 724 and 731a and stopcock assemblies 726 and 738. Stopcock assembly 726 consists of a 3-way valve 728, glass capillary tubing 730 and 734 in the main fluid system, and a section of glass capillary tubing 732 for replenishing reservoir 712 and forward flushing the fritted disc in fritted funnel 718. Stopcock assembly 738 similarly consists of a 3-way valve 740, glass capillary tubing 742 and 746 in the main fluid line, and a section of glass capillary tubing 744 that acts as a drain for the system.

Referring to FIG. 11, assembly 720 consists of a cylinder 754, a cup-like piston indicated by 756 and a weight 758 that fits inside piston 756. Attached to bottom end of cylinder 754 is a No. 400 mesh stainless steel cloth screen 759 that is biaxially stretched to tautness prior to attachment. Hydrogel-forming absorbent polymer indicated generally as 760 rests on screen 759. Cylinder 754 is bored from a transparent LEXAN® rod (or equivalent) and has an inner diameter of 6.00 cm (area=28.27 cm<sup>2</sup>), with a wall thickness of approximately 5 mm and a height of approximately 5 cm. The piston 756 is in the form of a Teflon cup and is machined to fit into cylinder 754 within tight tolerances. Cylindrical stainless steel weight 758 is machined to fit snugly within piston 756 and is fitted with a handle on the top (not shown) for ease in removing. The combined weight of piston 756 and weight

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758 is 1390 g, which corresponds to a pressure of 0.7 psi for an area of 28.27 cm<sup>2</sup>.

The components of apparatus 710 are sized such that the flow rate of synthetic urine therethrough, under a 10 cm hydrostatic head, is at least 0.01 g/cm<sup>2</sup>/sec, where the flow rate is normalized by the area of fritted funnel 718. Factors particularly impactful on flow rate are the permeability of the fritted disc in fritted funnel 718 and the inner diameters of glass tubing 724, 730, 734, 742, 746 and 731a, and stopcock valves 728 and 740.

Reservoir 712 is positioned on an analytical balance 716 that is accurate to at least 0.01 g with a drift of less than 0.1 g/hr. The balance is preferably interfaced to a computer with software that can (i) monitor balance weight change at pre-set time intervals from the initiation of the PUP test and (ii) be set to auto initiate on a weight change of 0.01-0.05 g, depending on balance sensitivity. Capillary tubing 724 entering the reservoir 712 should not contact either the bottom thereof or cover 714. The volume of fluid (not shown) in reservoir 712 should be sufficient such that air is not drawn into capillary tubing 724 during the measurement. The fluid level in reservoir 712, at the initiation of the measurement, should be approximately 2 mm below the top surface of fritted disc in fritted funnel 718. This can be confirmed by placing a small drop of fluid on the fritted disc and gravimetrically monitoring its slow flow back into reservoir 712. This level should not change significantly when piston/cylinder assembly 720 is positioned within funnel 718. The reservoir should have a sufficiently large diameter (e.g., ~14 cm) so that withdrawal of ~40 ml portions results in a change in the fluid height of less than 3 mm.

Jayco synthetic urine used in this test is prepared by dissolving a mixture of 2.0 g KCl, 2.0 g Na<sub>2</sub>SO<sub>4</sub>·0.85 g NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, 0.15 g (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, 0.19 g CaCl<sub>2</sub>, and 0.23 g MgCl<sub>2</sub> to 1.0 liters with distilled water. The salt mixture can be purchased from Endoventures, Reading, Pa. (cat no. JA-00131-000-01).

Prior to measurement, the assembly is filled with synthetic urine. The fritted disc in fritted funnel 718 is forward flushed so that it is filled with fresh synthetic urine. To the extent possible, air bubbles are removed from the bottom surface of the fritted disc and the system that connects the funnel to the reservoir. The following procedures are carried out by sequential operation of the 3-way stopcocks:

1. Excess fluid on the upper surface of the fritted disc is removed (e.g. poured) from fritted funnel 718.
2. The solution height/weight of reservoir 712 is adjusted to the proper level/value.
3. Fritted funnel 718 is positioned at the correct height relative to reservoir 712.
4. Fritted funnel 718 is then covered with fritted funnel cover 722.
5. The reservoir 712 and fritted funnel 718 are equilibrated with valves 728 and 740 of stopcock assemblies 726 and 738 in the open connecting position.
6. Valves 728 and 740 are then closed.
7. Valve 740 is then turned so that the funnel is open to the drain tube 744.
8. The system is allowed to equilibrate in this position for 5 minutes.
9. Valve 740 is then returned to its closed position.

Steps Nos. 7-9 temporarily "dry" the surface of fritted funnel 718 by exposing it to a small hydrostatic suction of ~5 cm. This suction is applied if the open end of tube



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**United States Patent** [19]

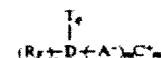
Milko et al.

[11] **Patent Number:** 5,731,095[45] **Date of Patent:** Mar. 24, 1998[54] **DENDRITIC POLYMER COATINGS**[75] **Inventors:** Larry A. Milko; Donald A. Tomalia,  
both of Midland, Mich.[73] **Assignee:** Oxazogen, Inc., Midland, Mich.[21] **Appl. No.:** 735,883[22] **Filed:** Oct. 23, 1996[51] **Int. Cl.<sup>6</sup>** ..... B32B 27/06; C08F 2/32;  
C08F 20/00[52] **U.S. Cl.** ..... 428/482; 528/288; 528/290;  
528/299; 528/401; 525/437; 525/440; 525/540;  
524/801; 524/802; 524/805; 524/839[58] **Field of Search** ..... 528/288, 290,  
528/299, 401; 525/437, 440, 540; 524/801,  
802, 805, 839; 428/482[56] **References Cited****U.S. PATENT DOCUMENTS**

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4,587,329	5/1986	Tomalia et al.	528/363
5,418,301	5/1995	Hult et al.	525/437

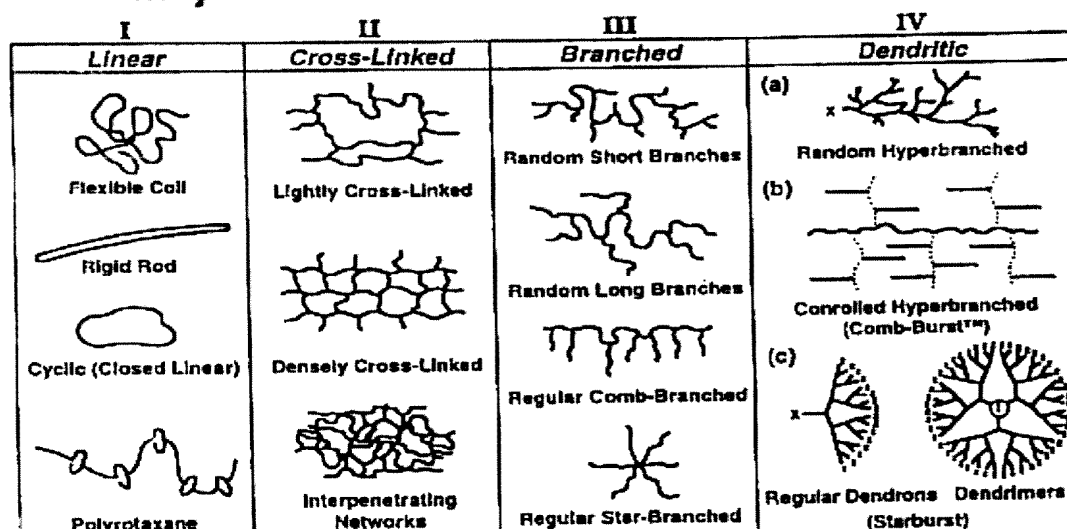
**Primary Examiner**—Samuel A. Acquah**Attorney, Agent, or Firm**—Price, Heneveld, Cooper, Dewitt & Litton[57] **ABSTRACT**

A water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one terminal fluorocarbon moiety and at least one terminal anionic moiety, and which is suitable for use in preparing protective coating compositions is disclosed. The water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants are represented by the general formula:



where D represents a dendritic polymer,  $R_F$  represents a fluorocarbon containing moiety,  $A^-$  represents an anionic containing moiety,  $C^+$  represents a cation, T represents a terminal group of the dendritic polymer which has not been functionalized with a fluorocarbon or anionic moiety, n and m are at least each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer. Also disclosed is a coating composition capable of forming a highly crosslinked, non-stick, protective coating. The coating composition includes a water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one terminal fluorocarbon moiety and at least one terminal anionic moiety, an oxazoline crosslinking agent, and a water-based solvent.

41 Claims, 1 Drawing Sheet

**Major Macromolecular Architectures**

1930's -

1940's -

1960's -

1980's -

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 (KIM & WEBSTER, ET AL.)  
 (TOMALIA, ET AL. & GAUTHIER, ET AL.)  
 (TOMALIA, ET AL. & FRECHET, ET AL.)

U.S. Patent

Mar. 24, 1998

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Major Macromolecular Architectures

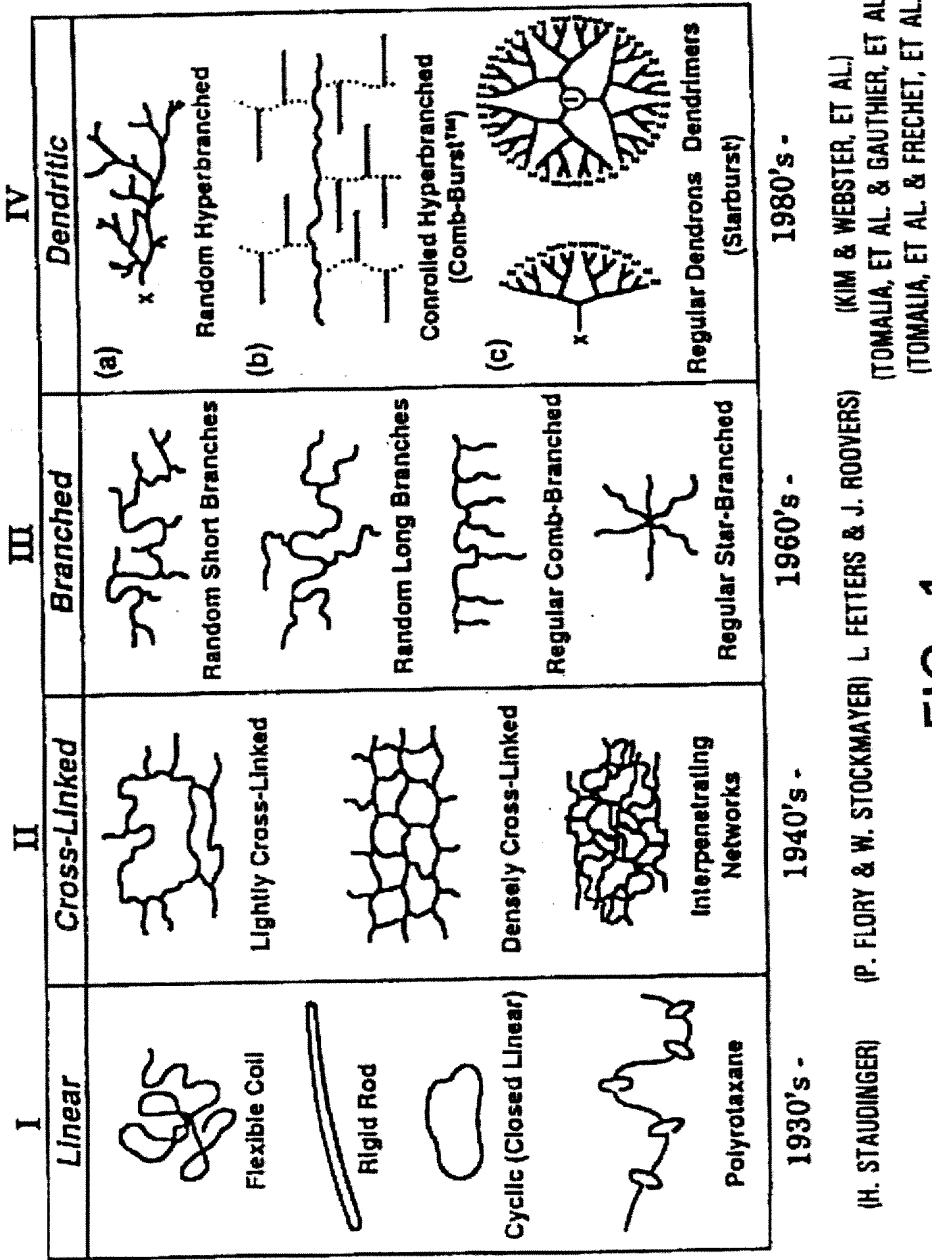


FIG. 1

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**DENDRITIC POLYMER COATINGS**

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of Contract No. DAAH04-96-C-0024 awarded by Department Of The Army.

**FIELD OF THE INVENTION**

This invention relates to water-based non-stick coating compositions derived from water-soluble or water-dispersible dendritic polymer surfactants containing pendant fluorocarbon groups and pendant chemically reactive anionic moieties. Such surfactants can be thermally crosslinked at low temperatures with an oxazoline crosslinking agent to form low-energy coatings which exhibit excellent anti-stick properties.

**BACKGROUND OF THE INVENTION**

There is a considerable demand for thin film coatings to which other substances will not adhere. Coatings are required to protect surfaces from soils, stains, ice, graffiti, insects, oils, corrosion, and chemical and biological contaminants. Moreover, as legislative pressures to remove volatile organic compounds (VOCs) from coating formulations persist, the demand for alternative water-borne systems continues to increase.

Compounds and polymer coatings containing fluorocarbon groups have been widely used for providing non-stick properties to surfaces. The foremost commercially available non-stick coating is polytetrafluoroethylene (PTFE). PTFE is characterized by a low surface free energy, excellent thermal stability, low coefficient of friction, anti-wetting properties, electrical insulation properties, and chemical inertness. However, because of its insolubility in most solvents, PTFE is relatively difficult to apply and is not very easily processed. Notably, conventional thermoplastic techniques are not applicable to PTFE. Rather, the material is most commonly applied by high temperature sintering processes (up to 400° C.). Also, PTFE exhibits poor adhesion to many substrates and is susceptible to wear and soiling. PTFE forms coating surfaces having microscopic pores into which various adhesives and foulant materials can permeate and become mechanically locked. As a result, PTFE does not form an effective non-stick surface against many types of materials, including adhesive marine materials and other biological foulants.

Recently, non-stick coatings have been prepared by crosslinking linear perfluoroalkyl polymeric surfactants containing pendant ionic moieties such as carboxylate with poly(2-isopropenyl-2-oxazoline). These coatings have the advantage of being soluble in predominately aqueous solvents. The thermally cured coatings provide non-wettable, hard polymer surfaces which are only slowly attacked by common organic solvents. However, prolonged cure times (several hours) are required to achieve highly crosslinked (e.g., 80%) coatings with optimum physical/chemical properties. Moreover, the excessive cure times associated with these coatings preclude widespread commercial utility.

Consequently, it would be desirable to provide low VOC non-stick coating formulations which cure rapidly at low temperatures to afford highly crosslinked non-stick coatings possessing excellent release properties.

**SUMMARY**

The present invention pertains to a water-soluble or water-dispersible fluorine-containing dendritic polymer sur-

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factant having at least one pendant fluorocarbon moiety and at least one pendant anionic moiety.

This invention also pertains to coating compositions comprising an aqueous solvent, a water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one pendant fluorocarbon moiety and at least one pendant anionic moiety, and a water-soluble or water-dispersible crosslinking agent having a plurality of oxazoline moieties which are capable of reacting with the anionic moiety of the dendritic polymer surfactant to form a crosslinked polymeric coating.

The non-stick coating compositions of this invention can be easily applied, such as with a brush, roller, spray gun, etc., and rapidly cured at a low temperature. Further, because the fluorine-containing dendritic polymer surfactants and coating compositions of this invention are water-soluble or water-dispersible, they can be formulated with low amounts of volatile organic solvents, whereby ease of application and rapid curing to form a hard, very low-porosity, non-stick coating is achieved while minimizing environmental and health hazards.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic illustration of the major macromolecular architectures.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The dendritic polymers which may be used in the practice of this invention include generally any of the known dendritic architectures including dendrimers, regular dendrons, controlled hyperbranched polymers, dendrigrafts, and random hyperbranched polymers. Dendritic polymers are polymers with densely branched structures having a large number of reactive groups. A dendritic polymer includes several layers or generations of repeating units which all contain one or more branch points. Dendritic polymers, including dendrimers and hyperbranched polymers, are prepared by condensation reactions of monomeric units having at least two different types of reactive groups. This fourth major class of polymer architecture is shown in FIG. 1.

Dendrimers are comprised of a plurality of dendrons that emanate from a common core which can be a single atom or a group of atoms. Each dendron generally consists of terminal surface groups, interior branch junctures having branching functionalities greater than or equal to two, and divalent connectors that covalently connect neighboring branching junctures. Dendrons and dendrimers can be prepared by convergent or divergent synthesis. Divergent synthesis of dendrons and dendrimers involves a molecular growth process which occurs through a consecutive series of geometrically progressive step-wise additions of branches upon branches in a radially outward molecular direction to produce an ordered arrangement of layered branch cells, in which each macromolecular includes a core cell, one or more layers of internal cells, and an outer layer of surface cells, wherein each of the cells includes a single branch juncture. The cells can be the same or different in chemical structure and branching functionality. The surface branch cells may contain either chemically reactive or passive functional groups. Chemically reactive surface groups can be used for further extension of dendritic growth or for modification of dendritic molecular surfaces. The chemically passive groups may be used to physically modify dendritic surfaces, such as to adjust the ratio of hydrophobic to hydrophilic terminals. Convergent synthesis of dendrim-



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ers and dendrons involves a growth process which begins from what will become the surface of the dendron or dendrimer and progresses radially in a molecular direction toward a focal point or cove.

Dendrons and dendrimers may be ideal or non-ideal, i.e., imperfect or defective. Imperfections are normally a consequence of either incomplete chemical reactions, or unavoidable competing side reactions. In practice, real dendritic polymers are generally non-ideal, i.e., contain certain amounts of structural imperfections.

A third method by which dendrimers and dendrons can be prepared is by using a one-pot synthesis in which dendritic polymers are prepared by a step-growth polymerization reaction of a single type of monomer having a single reactive group of a first type (B) and a plurality (y) of reactive groups of a second type (A), i.e., a B-A<sub>y</sub> type monomer, which is initiated by a core having a plurality (x) of the A type reactive groups, wherein A groups can react with B groups, but not with other A groups, and B groups cannot react with other B groups. The one-pot synthesis method is simpler and less expensive than the divergent and convergent synthesis methods. However, the one-pot synthesis method lacks reaction control, which leads to more polydispersed products with larger deviations from ideal dendron structure.

Hyperbranched polymers represent a class of dendritic polymers which contain high levels of non-ideal irregular branching arrays as compared with the more nearly perfect regular structure of dendrons and dendrimers. Specifically, hyperbranched polymers contain a relatively high number of irregular branching arrays in which not every repeat unit contains a branch juncture. Consequently, hyperbranched polymers may be viewed as intermediate between randomly branched polymers and regular dendrons and dendrimers, yet dendritic, because of their relatively high branch-juncture content per individual macromolecule.

The preparation and characterization of dendrimers, dendrons, random hyperbranched polymers, controlled hyperbranched polymers, and dendrigrafts is well known. Examples of dendrimers and dendrons, and methods of synthesizing the same are set forth in U.S. Pat. Nos. 4,507,466; 4,558,120; 4,568,737; 4,587,329; 4,631,337; 4,694,064; 4,713,975; 4,737,550; 4,871,779 and 4,857,599. Examples of hyperbranched polymers and methods of preparing the same are set forth, for example, in U.S. Pat. No. 5,418,301.

More generally dendritic polymers or macromolecules are characterized by a relatively high degree of branching (DB), which is defined as the number average fraction of branching groups per molecule, i.e., the ratio of terminal groups plus branch groups to the total number of terminal groups, branch groups and linear groups. For ideal dendrons and dendrimers the degree of branching is one. For linear polymers the degree of branching is zero. Hyperbranched polymers have a degree of branching which is intermediate between that of linear polymers and ideal dendrimers. The dendritic polymers used in this invention desirably have a degree of branching which is at least equal to or greater than 0.1, more preferably greater than or equal to 0.4, and most preferably greater than 0.5.

Dendritic polymers suitable for use with the invention also include macromolecules commonly referred to as cascade molecules, arborols, arborescent grafted molecules, and the like. Suitable dendritic polymers also include bridged dendritic polymers (i.e., dendritic macromolecules linked together either through surface functional groups or through a linking molecule connecting surface functional

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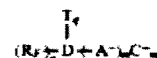
groups together) and dendritic polymer aggregates. The dendritic polymer used in the practice of this invention can be generationally monodisperse or generationally polydisperse solutions. Dendritic polymers in a monodisperse solution are substantially all of the same generation, and hence of uniform size and shape. The dendritic polymers in the polydisperse solution comprise a distribution of different generation polymers. Furthermore, the dendritic polymer molecules may be mixtures of different interior and exterior composition or functionality.

Generally, any of the known dendritic polymers having anionic terminal groups, or having terminal groups which can be reacted with another compound to provide anionic terminal groups, are suitable for use in preparing the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants and coating compositions of this invention. Examples of suitable dendritic polymers include poly(ether) dendrons, dendrimers and hyperbranched polymers, poly(ester) dendrons, dendrimers and hyperbranched polymers, poly(thioether) dendrons, dendrimers and hyperbranched polymers, poly(arylalkylene) dendritic polymers, etc.

While generally any dendritic polymer can be used in the preparation of the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants of this invention, it is desirable to avoid the use of dendritic polymers which are at least as basic as the oxazoline moieties of the crosslinking agent in the coating compositions of this invention because they tend to inhibit proton transfer to the oxazoline functional moieties and consequently inhibit crosslinking. Examples of dendritic polymers which tend to inhibit protonation of the oxazoline moieties include generally any of the amine containing dendrimers, such as the polyamidoamine (PAMAM) dendritic polymers.

The terminal or surface reactive groups of the dendritic polymers which are used to prepare the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants used in the preparation of non-stick coatings in accordance with this invention include any nucleophilic or electrophilic group which is capable of forming covalent bonds with a fluorine-containing compound and an anionic moiety-containing compound to afford a dendritic polymer surfactant.

The water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants suitable for preparing the non-stick coatings of this invention are represented by the general formula



where D represents a dendritic polymer, R<sub>f</sub> represents a fluorocarbon-containing moiety, A<sup>-</sup> represents an anionic containing moiety, C<sup>+</sup> represents a cation, T represents a terminal group which has not been functionalized with a fluorocarbon or anionic moiety, n and m are each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer.

Hydroxy-terminated hyperbranched polyesters are presently preferred starting materials for the preparation of water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants in accordance with the invention because of their relatively low cost and commercial availability. Suitable hydroxy-terminated hyperbranched polyesters for use in the manner of this invention include first through fourth generation polymers having molecular



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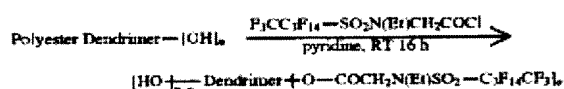
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weights ranging from about 1,500 to about 8,000, and having from about 16 to about 64 terminal hydroxy groups.

The fluorine-containing dendritic polymer surfactants which are employed in the coating compositions of this invention are provided with at least one pendent fluorocarbon moiety and at least one pendent anionic moiety.

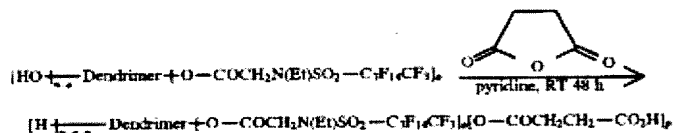
The fluorocarbon moiety is a linear or branched fluoroalkyl group having at least one terminal trifluoromethyl group and containing at least three fully fluorinated carbon atoms. Preferred fluoroalkyl moieties are fully fluorinated alkyls, i.e., perfluoroalkyls.

Fluorocarbon moieties can be introduced into a dendritic polymer by reacting the dendritic polymer with a fluorine-containing compound having a fluoroalkyl moiety and a reactive linking moiety capable of covalently bonding to the reactive terminal groups of the dendritic polymer. For example, a hydroxy-terminated hyperbranched polyester can be reacted with a fluorine-containing acyl halide in the presence of a suitable solvent, such as pyridine, for a suitable period of time (e.g., 16 hours) at room temperature to form a perfluoroalkyl-terminated hyperbranched polyester as follows:



where  $n$  is the total number of terminal groups on the dendritic polymer and  $O$  is the number of fluoroalkyl-containing terminal moieties.

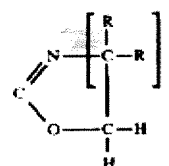
Preferred anionic moieties include carboxylate groups and thiol groups, with carboxylate terminal moieties being most preferred. Anionic moieties can be covalently bonded to the reactive terminals of the dendritic polymer by reacting a anionic moiety-containing compound or a compound capable of forming an anionic moiety with the reactive terminal groups of the dendritic polymer. For example, terminal carboxyl moieties can be introduced into a hydroxy-terminated dendritic polymer by reacting the terminal hydroxy groups with an anhydride of a dicarboxylic acid. For instance, the above perfluoroalkyl-terminated hyperbranched polyester can be reacted with succinic anhydride at room temperature for a suitable period of time (e.g., 48 hours) in a suitable solvent (e.g., pyridine) to form a carboxyl/perfluoroalkyl terminated hyperbranched polyester as follows:



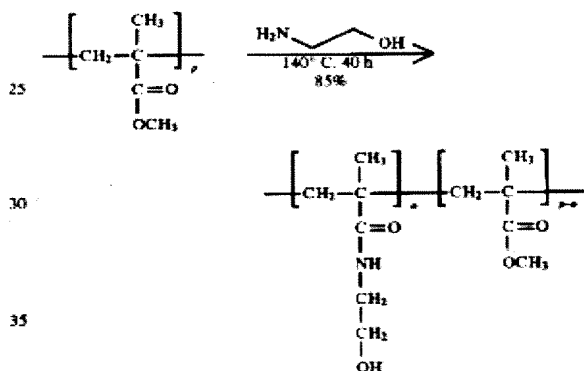
The number of anionic terminal moieties and perfluoroalkyl terminal moieties can be varied as desired to provide custom tailored properties for particular applications. In general, higher levels of anionic terminal moieties provide better water-solubility or water-dispersibility.

The crosslinking compounds used in the preparation of coating compositions in accordance with this invention are compounds containing a plurality (at least two) of oxazoline moieties represented by the formula

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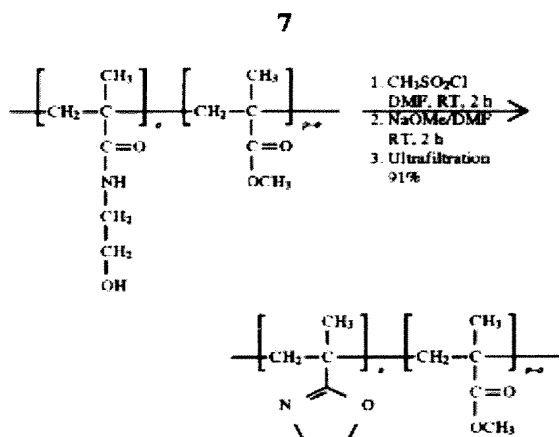
where each  $R$  is a hydrogen atom, a hydroxy methyl group or an organic radical, and  $k$  is 1 or 2, most preferably 1. Preferred oxazoline crosslinking agents include polymeric compounds containing pendant oxazolines moieties, such as poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate), poly(IPO/MMA). For example, suitable polymeric oxazoline crosslinking agents can be prepared by reacting a polyacrylate, such as poly(methyl methacrylate), with ethanolamine, e.g., at  $140^\circ\text{C}$ . for 40 hours in an aminolysis reaction, to produce an acrylic polymer having pendant hydroxy groups as follows:



where  $P$  is the total number of acrylate units or monomers in the polyacrylate and  $o$  is the number of acrylate units which have been reacted. The above amidated polyacrylate is subsequently subjected to conditions which cause the pendant hydroxyethylamide moieties to undergo ring formation to form oxazoline moieties. For example, in the presence of  $\text{CH}_3\text{SO}_2\text{Cl}$  in a suitable solvent, such as DMF, the pendant hydroxyethylamide groups are converted into oxazoline moieties at room temperature in about 2 hours to

form an acrylic polymer having pendant oxazoline moieties as follows:

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Coating formulations in accordance with the invention are prepared by combining the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactants and oxazoline crosslinking agents in water or in an aqueous solution comprised primarily of water and containing a minor amount of an organic solvent. Organic cosolvents are generally not preferred, although small amounts, i.e., 20 percent by weight or less, may be added to aid curing.

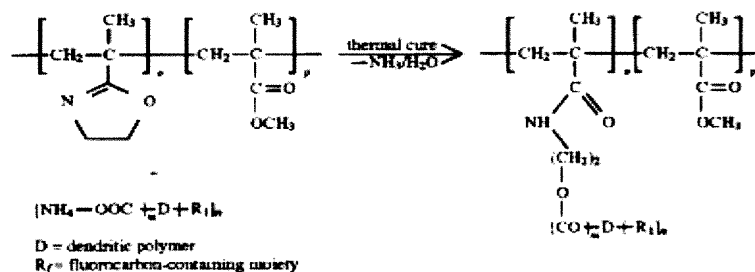
The coating compositions of this invention can be applied by generally any conventional method, such as those used to apply paint to surfaces. Suitable techniques for applying the coatings of this invention include wiping, brushing, spraying, dipping, and spin-coating. Suitable substrates for the coatings of this invention include metal, plastic, glass, masonry, paper and textiles. Any suitable heating method may be used to cure the coatings, such as radiant heating and heated air.

The coating compositions of this invention are extremely stable, i.e., crosslinking does not occur to any appreciable extent during storage of the coating compositions in a sealed container.

After application, the coating compositions of this invention cure very rapidly at relatively low temperatures, e.g., typically over 80% cure in 15 minutes or less at a temperature of 110° C. The coating compositions of the invention also have the advantage of being non-flammable, and have very low or no volatile organic compounds (VOCs).

Curing of the coating compositions of this invention occurs upon application of heat by reaction of the oxazoline moieties of the crosslinking agent with the anionic groups of the water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant. For example:

PREPARATION OF WATER-BORNE NON-STICK COATINGS:  
CROSSLINKING REACTION



Examples of suitable cosolvents include ethylene glycol, propylene glycol, and the like. The concentrations of the formulation can typically range from about 0.01 to about 60 weight percent solids (i.e., the dendritic polymer surfactant and oxazoline crosslinker constitute from about 0.01 to about 60% of the composition by weight) and more preferably from about 1.0 to about 25 weight percent solids (i.e., from 1 to 25 weight percent dendritic polymer surfactant and oxazoline crosslinker). The preferred concentrations will depend on such factors as the desired viscosity, coating thickness and method of application. The amounts of water-dispersible or water-soluble fluorine-containing dendritic polymers and oxazoline crosslinking agents are selected so that the mole ratio of oxazoline moieties to anionic moieties is preferably about 1:1, for example, from about 0.8:1 to about 1.2:1. Lower or higher ratios provide coatings with more hydrophilic surfaces. The pH of the aqueous formulation is preferably kept slightly basic to avoid acid catalyzed hydrolysis of the oxazoline groups in the crosslinking agent. The pH of the formulation is preferably adjusted to a range of from about 7 to about 8. However, the preferred pH will depend on the pH stabilities of other functional groups present in the polyoxazoline and fluorine-containing dendritic polymer surfactant. The preferred cation, C<sup>+</sup>, include ammonium and low molecular weight protonated amines.

### EXAMPLE 1

#### Preparation of Carboxy/Perfluoroalkyl-Terminated Hyperbranched Polymers

Perstorp polyol and pyridine were combined in a 100 ml round bottom flask under nitrogen. The mixture became homogeneous after stirring at room temperature for 2 hours. To the vigorously stirred mixture was added a solution of C<sub>6</sub>F<sub>17</sub>SO<sub>2</sub>N(Et)CH<sub>2</sub>COCl in dry acetone (38% w/w) at a rate of 0.5 ml/minute using a syringe pump. The mixture was then stirred overnight at room temperature. Succinic anhydride was added to the solution in a single portion. After 48–72 hours, the reaction mixture was diluted with methanol (150 ml) and purified by ultrafiltration employing a tangential flow device (Amicon) equipped with a MWco=1000 membrane (Amicon YM1). After 8 retentate volumes of permeate were obtained, the retentate was concentrated under reduced pressure using a rotary evaporator. The residue was evacuated under high vacuum at room temperature to afford a viscous liquid. The mole percent of terminal carboxyl groups and terminal perfluoroalkyl groups were determined from the <sup>1</sup>H NMR spectrum of the product (300 MHz, acetone-d<sub>6</sub>/TMS). The mole percent of terminal carboxyl groups was determined from the ratio of the integrated

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intensities of the signals at  $\delta$  2.6 (br s,  $\text{COCH}_2\text{CH}_2\text{CO}$ ) and  $\delta$  3.5–3.7 (complex,  $\text{CH}_2\text{OH}$ ). The mole percent of terminal perfluoroalkyl groups was determined from the ratio of integrated intensities of the signals at  $\delta$  2.6 (br s,  $\text{COCH}_2\text{CH}_2\text{CO}$ ) and  $\delta$  4.2–4.4 (complex,  $\text{CH}_2\text{O}-\text{CO}$  and  $\text{N}-\text{CH}_2$ ).

Products derived from generation 2, 3, and 4 hyperbranched polyesters were prepared using the quantities of reagents specified in Table 1.

## EXAMPLE 2

## Preparation of poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate)

A 5 liter 3-neck round bottom flask was equipped with a reflux condenser, mechanical stirrer (teflon blade), and a thermometer attached to a Therm-o-Watch temperature controller. To the flask was added poly(methyl methacrylate) (MW=75,000, 500 g, 5 moles ester) and ethanolamine (2443 g, 40 moles) under nitrogen. The mixture was stirred and heated at  $150^\circ\text{C}$ . for 35 hours and then allowed to cool to room temperature. The mixture was diluted with methanol (5 liters) and added dropwise to 3 volumes of mechanically stirred toluene. After completion of the addition, the mixture was allowed to stand undisturbed for 10 minutes. The supernatant liquid was decanted and the residue was washed twice with toluene ( $2 \times 300\text{ mL}$ ). The residue was dissolved in methanol (3 liters) and added dropwise to three times the volume of stirred toluene. The precipitate was collected in a Buchner funnel and washed twice with toluene ( $2 \times 200\text{ mL}$ ). Drying overnight under high vacuum at  $50^\circ\text{C}$ . afforded poly(2-hydroxyethylmethacrylamide-co-methyl methacrylate) (550 g, 85%).

To a 1 liter 3 neck round bottom flask equipped with a mechanical stirrer was added poly(2-hydroxyethylmethacrylamide-co-methyl methacrylate) (52 g, 403 mmole OH) and dimethylformamide (DMF, 300 mL) under nitrogen. The stirred mixture was heated at  $150^\circ\text{C}$ . until complete dissolution occurred and then allowed to cool to room temperature. The stirred mixture was treated with methanesulfonyl chloride (58 g, 506 mmole) and heated at  $100^\circ\text{C}$ . until homogeneous. The mixture was then stirred an additional 2 hours at room temperature. The mixture was diluted with DMF (50 mL) and added during a 10 minute period to a solution of sodium methoxide (101 g, 1.87 mole) in DMF (100 mL) under nitrogen. After stirring for 2 hours at room temperature, most of the solvent was removed by vacuum distillation (1–5 mmHg,  $80^\circ\text{--}150^\circ\text{C}$ ). The resulting residue was dissolved in methanol (3 liters) and ultrafiltered using a tangential ultrafiltration system (Amicon B6) equipped with regenerated cellulose membrane (MWCO=3000,  $4.2\text{ ft}^2$ ). After 8 retentate volumes of permeate were collected, the retentate was filtered through Whatman No.1 paper. The filtrate was concentrated under reduced pressure using a rotary evaporator. The residue was evacuated at high vacuum for 18 hours to afford the desired product (41 g, 91%) as a slightly brown solid. The mole percentage of oxazoline was determined to be 86%, based on the integrated intensities of the oxazoline  $\text{CH}_2$  (multiplets,  $\delta$  3.77 and 4.28, 4H) and ester  $\text{CH}_3$  (s,  $\delta$  3.63, 3H) signals in the  $^1\text{H}$ NMR spectrum (300 MHz,  $\text{CD}_3\text{OD/TMS}$ ) of the product.

## EXAMPLE 3

## Formulation of Coatings

The carboxy/perfluoroalkyl-terminated hyperbranched polyester was dissolved in isopropanol (30% w/w). The pH

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of the solution was adjusted to 7–8 with ammonium hydroxide (1N). To the solution was added an aqueous solution of polyIPO/MMA (10% w/w, 7.85 mmoles oxazoline/g polymer) in an amount required to achieve a 1:1 mole ratio of oxazoline/ $\text{CO}_2\text{H}$ . Ethylene glycol was added to the mixture in an amount equal to the combined weight of hyperbranched polymer and polyIPO/MMA. The mixture was then diluted with deionized water to achieve a final concentration of 10–12% w/w solids. The mixture was stirred until homogeneous and then filtered ( $0.5\text{ }\mu\text{m}$ ).

## EXAMPLE 4

## Application of Coatings to Substrates

Each coating formulation was applied to a single infrared AgCl crystal window ( $2.5 \times 2.5 \times 0.1\text{ cm}$ ) and a glass microscope slide ( $25 \times 75 \times 1\text{ mm}$ ) with a Paul-Gardner wire-wound film applicator (AP-FD02.5, wire #2.5) for determination of the extent of crosslinking and contact angle measurements, respectively.

## EXAMPLE 5

## Thermal Cure of Coatings

Freshly coated substrates were cured in an oven at  $110^\circ\text{C}$ . The infrared windows were removed from the oven following cumulative cure times of 0.25 h, 0.5 h, 0.75 h, 1 h, 4 h, 10 h, 24 h, and 46 h (or 48 h). The windows were allowed to cool to room temperature prior to spectrometric analysis. The coated glass slides were removed from the oven after 1 hour of cure and allowed to cool to room temperature prior to contact angle measurements.

## EXAMPLE 6

## Determination of the Extent of Crosslinking in Coatings

The extent of crosslinking in the coatings was determined by monitoring the amide  $\text{N}-\text{H}$ , amide  $\text{C}=\text{O}$ , and oxazoline  $\text{C}=\text{N}$  stretching absorptions using FTIR spectrometry. Spectra were recorded on a Nicolet FTIR spectrometer and analyzed using OMNIC FTIR software. FTIR spectra of the cured films feature an amide  $\text{N}-\text{H}$  stretching absorption in the region from  $1500$  to  $1550\text{ cm}^{-1}$  and overlapping amide  $\text{C}=\text{O}$  and oxazoline  $\text{C}=\text{N}$  stretching absorptions in the region from  $1580$  to  $1680\text{ cm}^{-1}$ . The extent of crosslinking in cured coatings was calculated using equation 1:

$$\text{Extent of crosslinking, \%} = \quad (1)$$

$$\frac{A_{\text{amide N-H}} \cdot \mathcal{A}_{\text{amide C=O}} - A_{\text{amide C=O}} \cdot \mathcal{A}_{\text{amide N-H}}}{A_{\text{amide C=O}} \cdot \mathcal{A}_{\text{oxazoline C=N}} - A_{\text{oxazoline C=N}} \cdot \mathcal{A}_{\text{amide C=O}}} \times 100$$

here  $A_{\text{amide N-H}}$  is the integrated amide  $\text{N}-\text{H}$  absorbance,  $A_{\text{amide C=O}}$  is the integrated amide  $\text{C}=\text{O}$  absorbance,  $A_{\text{oxazoline C=N}}$  is the integrated oxazoline  $\text{C}=\text{N}$  absorbance,  $\mathcal{A}_{\text{amide N-H}}$  is the absorptivity of the amide  $\text{N}-\text{H}$  stretching absorption.

$\mathcal{A}_{\text{amide C=O}}$  is the absorptivity of the amide  $\text{C}=\text{O}$  stretching absorption, and  $\mathcal{A}_{\text{oxazoline C=N}}$  is the absorptivity of the oxazoline  $\text{C}=\text{N}$  stretching absorption. Absorptivities for the amide  $\text{N}-\text{H}$ , amide  $\text{C}=\text{O}$ , and oxazoline  $\text{C}=\text{N}$  stretching absorptions were derived from the slopes of absorbance versus concentration plots for the model compounds poly[N-(2-hydroxyethyl) methacrylamide-co-methyl methacrylate], N-(2-hydroxyethyl)-2,2-

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dimethylpropanamide, and poly(2-isopropenyl-2-oxazoline-co-methyl methacrylate), respectively. The absorptivity of the amide N—H stretching absorption is  $8 \times 10^5$  cm/mole in the range from 1500–1550  $\text{cm}^{-1}$ . The absorptivities of the amide C=O and oxazoline C=N stretching absorptions are  $1.81 \times 10^7$  cm/mole and  $1.58 \times 10^7$  cm/mole in the range from 1580–1680  $\text{cm}^{-1}$ .

The results of cure studies employing hyperbranched polymer coatings are shown in Table 2.

## EXAMPLE 7

## Contact Angle Measurements

The contact angles of deionized water and hexadecane (Aldrich, 90+%) on cured coatings were determined using a Rame-Hart goniometer (Model A-100). The liquid drops were applied using a microliter syringe (Gilmont). The advancing contact angle of water was measured on a 50  $\mu\text{l}$  water droplet and the receding contact angle was measured after 30  $\mu\text{l}$  of water was withdrawn from the droplet. The advancing contact angle of hexadecane was measured on a 5  $\mu\text{l}$  droplet and the receding contact angle was measured following the withdrawal of 3  $\mu\text{l}$  of hexadecane from the droplet.

The results of contact angle measurements performed on hyperbranched polymer coatings are provided in Table 3.

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TABLE 2-continued

Curing of Hyperbranched Polymer Coatings†					
Hyperbranched Polymer Surfactant					
Coat- ing	Gene- ration	mole % $R_f$	mole % $\text{CO}_2\text{H}$	Cure Time hours	Crosslinking %
3	3	64	46	0.25	82
				0.5	88
				0.75	88
				1	89
				2	91
4	3	40	31	4	94
				10	99
				24	100
				48	99
				0.25	86
5	4	51	63	0.5	91
				0.75	94
				1	96
				2	97
				4	100
5	4	51	63	10	99
				24	98
				46	97
				0.25	76
				0.5	79
				0.75	81

TABLE 1

Preparation of Carboxy/Perfluoroalkyl-Terminated Hyperbranched Polymers

Hyperbranched Polymer				$\text{C}_6\text{H}_4\text{SO}_3\text{N}(\text{Et})\text{CH}_2\text{COCl}$		Succinic Anhydride		Pyridine	Product Composition	
Preparation	Generation	grams	mmoles OH	grams	mmoles	grams	mmoles	ml	mole % $R_f$	mole % $\text{CO}_2\text{H}$
1	2	1.90	17.1	0.85	1.40	3.10	30.0	14.0	12	56
2	2	1.30	11.7	2.17	3.60	1.50	15.0	10.0	22	36
3	3	2.82	24.7	1.21	2.00	2.50	25.0	25.0	5.4	46
4	3	3.16	27.7	8.80	14.6	2.80	28.0	28.0	40	31
5	4	3.00	26.0	1.28	2.12	3.00	30.0	25.0	5.1	63
6	4	3.00	26.0	4.83	8.00	3.00	30.0	25.0	25.0	48

 $R_f = -\text{C}_6\text{F}_{13}$ 

TABLE 2

Curing of Hyperbranched Polymer Coatings†					
Hyperbranched Polymer Surfactant					
Coat- ing	Gene- ration	mole % $R_f$	mole % $\text{CO}_2\text{H}$	Cure Time hours	Crosslinking %
1	2	12	56	0.25	83
				0.5	88
				0.75	89
				1	90
				2	93
				4	94
				10	96
				24	97
				46	99
				0.25	81
2	2	22	36	0.5	89
				0.75	91
				1	93
				2	97
				4	100
				10	100
				24	95
				46	97

TABLE 2-continued

Curing of Hyperbranched Polymer Coatings†					
Hyperbranched Polymer Surfactant					
Coat- ing	Gene- ration	mole % $R_f$	mole % $\text{CO}_2\text{H}$	Cure Time hours	Crosslinking %
50	6	25	48	1	82
				2	86
				4	87
				10	91
				24	95
				48	97
				0.25	82.2
				0.5	87
				0.75	88
				1	91
60	6	25	48	2	93
				4	96
				10	97
				24	99.6
				48	100

Coatings cured at 110° C.  
 $R_f = -\text{C}_6\text{F}_{13}$

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TABLE 3

Physical Properties of Hyperbranched Polymer Coatings <sup>a</sup>							
Hyperbranched Polymer Surfactant				Contact Angle, degrees			
Coating	Generation	mole % R <sub>f</sub>	mole % CO <sub>2</sub> H	Θ <sub>h</sub> water	Θ <sub>i</sub> water	Θ <sub>h</sub> hexadecane	Θ <sub>i</sub> hexadecane
1	2	12	56	112	85	61	61
2	2	22	36	111	84	66	65
3	3	6.4	46	112	81	66	66
4	3	40	31	115	89	68	67
5	4	5.1	63	115	88	68	67
6	4	25	48	106	79	68	65

<sup>a</sup>Coatings cured at 110° C. for 1 hourR<sub>f</sub> = - C<sub>8</sub>F<sub>17</sub>

It will be apparent to those skilled in the art that various modifications to the preferred embodiment of the invention as described herein can be made without departing from the spirit or scope of the invention as defined by the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one pendant fluorocarbon moiety and at least one pendant anionic moiety.

2. The dendritic polymer surfactant of claim 1 represented by the formula



where D represents a dendritic polymer, R<sub>f</sub> represents a fluorocarbon-containing moiety, A<sup>-</sup> represents an anionic-containing moiety, C<sup>+</sup> represents a cation, T represents a terminal group of the dendritic polymer which has not been functionalized with a fluorocarbon or anionic moiety, n and m are each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer.

3. The dendritic polymer surfactant of claim 2, wherein the dendritic polymer is a dendron or dendrimer.

4. The dendritic polymer surfactant of claim 2, wherein the dendritic polymer is a hyperbranched polyester.

5. The dendritic polymer surfactant of claim 2, wherein the fluorocarbon-containing moiety includes a linear or branched fluoroalkyl group having at least one terminal trifluoromethyl group and containing at least three fully fluorinated carbon atoms.

6. The dendritic polymer surfactant of claim 2, wherein the fluorocarbon-containing moiety includes a perfluoroalkyl group.

7. The dendritic polymer surfactant of claim 2, wherein the fluorocarbon-containing moiety is represented by the formula—COCH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)SO<sub>2</sub>(C<sub>7</sub>F<sub>14</sub>CF<sub>3</sub>).

8. The dendritic polymer surfactant of claim 2, wherein the anionic-containing moiety includes a carboxylate group.

9. The dendritic polymer surfactant of claim 2, wherein the T groups are hydroxy groups.

10. The dendritic polymer surfactant of claim 2, wherein the cation is ammonium.

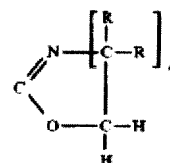
11. The dendritic polymer surfactant of claim 2, wherein the cation is a low molecular weight protonated amine.

12. A non-stick coating composition comprising:

a water-soluble or water-dispersible fluorine-containing dendritic polymer surfactant having at least one pen-

dant fluorocarbon moiety and at least one pendant anionic moiety;

a crosslinking compound containing a plurality of oxazoline or oxazine moieties represented by the formula



where each R is a hydrogen atom, a hydroxy methyl group or an organic radical, and k is one or two; and

an aqueous solvent comprising primarily water and optionally containing a minor amount of an organic solvent.

13. The coating composition of claim 12, wherein the dendritic polymer surfactant is represented by the formula



where D represents a dendritic polymer, R<sub>f</sub> represents a fluorocarbon containing moiety, A<sup>-</sup> represents an anionic-containing moiety, C<sup>+</sup> represents a cation, T represents a terminal group of the dendritic polymer which has not been functionalized with a fluorocarbon or anionic moiety, n and m are each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer.

14. The coating composition of claim 13, wherein the T groups are hydroxy groups.

15. The coating composition of claim 13, wherein the dendritic polymer is a hyperbranched polyester.

16. The coating composition of claim 13, wherein the fluorocarbon moiety is a linear or branched fluoroalkyl group having at least one terminal trifluoromethyl group and containing at least three fully fluorinated carbon atoms.

17. The coating composition of claim 16, wherein the anionic-containing moiety includes a carboxylate group.

18. The coating composition of claim 13, wherein the oxazoline crosslinking agents include polymeric compounds containing pendant oxazoline moieties.

19. The coating composition of claim 18, wherein the oxazoline crosslinking agent is an acrylate polymer having pendant oxazoline moieties.

20. The coating composition of claim 13, wherein the dendritic polymer surfactant and oxazoline crosslinking agent comprise from about 0.01 to about 60% of the composition by weight.

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21. The coating composition of claim 20, wherein the amounts of fluorine-containing dendritic polymers and oxazoline crosslinking agents are selected so that the mole ratio of oxazoline moieties to anionic moieties is from about 0.8:1 to about 1.2:1.

22. The coating composition of claim 13, wherein the pH is from about 7 to about 8.

23. The coating composition of claim 13, wherein the fluorocarbon-containing moiety includes a perfluoroalkyl group.

24. The coating composition of claim 13, wherein the fluorocarbon-containing moiety is represented by the formula  $-\text{COCH}_2\text{N}(\text{C}_2\text{H}_5)\text{SO}_2(\text{C}_7\text{F}_{14}\text{CF}_3)$ .

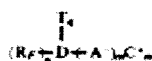
25. The coating composition of claim 13, wherein the anionic-containing moiety includes a carboxylate group.

26. The coating composition of claim 13, wherein the cation is ammonium.

27. The coating composition of claim 13, wherein the cation is a low molecular weight protonated amine.

28. A highly crosslinked protective coating comprising a reaction product of a dendritic polymer surfactant having at least one pendant fluorocarbon moiety and at least one pendant anionic moiety and an oxazoline crosslinking agent.

29. The coating of claim 28, wherein the dendritic polymer surfactant is represented by the formula



where D represents a dendritic polymer,  $\text{R}_f$  represents a fluorocarbon containing moiety,  $\text{A}^-$  represents an anionic-containing moiety,  $\text{C}^+$  represents a cation, T represents a terminal group of the dendritic polymer which has not been functionalized with a fluorocarbon or anionic moiety, n and m are each at least one, and the sum of n+m+q is the total number of terminal groups on the dendritic polymer.

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30. The coating of claim 29, wherein the F groups are hydroxy groups.

31. The coating of claim 29, wherein the dendritic polymer is a hyperbranched polyester.

32. The coating of claim 29, wherein the fluorocarbon moiety is a linear or branched fluoroalkyl group having at least one terminal trifluoromethyl group and containing at least three fully fluorinated carbon atoms.

33. The coating of claim 31, wherein the anionic-containing moiety includes a carboxylate group.

34. The coating of claim 29, wherein the oxazoline crosslinking agents include polymeric compounds containing pendant oxazoline moieties.

35. The coating of claim 34, wherein the oxazoline crosslinking agent is an acrylate polymer having pendant oxazoline moieties.

36. The coating of claim 35, wherein the amounts of fluorine-containing dendritic polymers and oxazoline crosslinking agents are selected so that the mole ratio of oxazoline moieties to anionic moieties is from about 0.8:1 to about 1.2:1.

37. The coating of claim 29, wherein the fluorocarbon-containing moiety includes a perfluoroalkyl group.

38. The coating of claim 29, wherein the fluorocarbon-containing moiety is represented by the formula  $-\text{COCH}_2\text{N}(\text{C}_2\text{H}_5)\text{SO}_2(\text{C}_7\text{F}_{14}\text{CF}_3)$ .

39. The coating of claim 29, wherein the anionic-containing moiety includes a carboxylate group.

40. The coating of claim 29, wherein the cation is ammonium.

41. The coating of claim 29, wherein the cation is a low molecular weight protonated amine.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 5,731,095

DATED : March 24, 1998

INVENTOR(S) : Larry A. Milco and Donald A. Tomalia

Page 1 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Abstract, line 15;

Delete "at least" (1st occurrence).

Column 2, line 56;

"macromolecular" should be ~~macromolecule~~.

Column 3, line 4;

"cove" should be ~~core~~.

\*Column 5, line 36;

"a" (1st occurrence) should be ~~an~~.

Column 5, After line 55,(2nd equation);

"[H]<sub>nop</sub> Dendrimer (etc.)" should be

~~-[HO]<sub>nop</sub> Dendrimer (etc.)~~.

Column 6, line 13

"oxazolines" should be ~~oxazoline~~.

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 5,731,095

DATED : March 24, 1998

INVENTOR(S) : Larry A. Milco and Donald A. Tomalia

Page 2 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Columns 11 & 12, Table 2, line 2 of the 3 Sections, Subheadings;

"Hyperbranced" should be -Hyperbranched-.

Column 16, claim 32, line 7;

"trifluoromethyl" should be -trifluoromethyl-.

Signed and Sealed this  
First Day of September, 1998

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks



**RELATED PROCEEDINGS APPENDIX**

None.